

THE SPATIAL VARIABILITY OF SOIL PROPERTIES  
AND 2,4-D SORPTION AND DESORPTION IN  
TWO CALCAREOUS PRAIRIE LANDSCAPES

BY

KRISTIAN DIETRICH STEPHENS

A Thesis  
Submitted to the Faculty of Graduate Studies  
In Partial Fulfillment of the Requirements  
for the Degree of

MASTER OF SCIENCE

Department of Soil Science  
University of Manitoba  
Winnipeg, Manitoba

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## ABSTRACT

Stephens, Kristian Dietrich. M.Sc., The University of Manitoba, October, 2003. The Spatial Variability of soil Properties and 2,4-D Sorption and Desorption in two Calcareous Prairie Landscapes. Major Professor; Annemieke Farenhorst.

Pesticides are widely used worldwide to increase agricultural crop yields, in which most of the applied pesticides are herbicides. Following application, herbicide sorption and desorption are the two most important processes controlling the herbicide's behaviour in the environment.

This study examined the effects that soil properties and tillage have on the spatial variability of 2,4-Dichlorophenoxyacetic acid (2,4-D) sorption and desorption which may be useful for landscape based agricultural management and for pesticide fate modeling. The two agricultural sites were a heavily-tilled eroded hummocky landscape near Morris, Minnesota and a glacial till undulating landscape near Miniota, Manitoba. The herbicide sorption and desorption experiments were determined by the standard batch equilibrium method which used  $^{14}\text{C}$  labeled 2,4-D solutions.

Both landscapes were delineated into landform element complexes (LECs) by a landform description model for describing the spatial distribution of the soil properties and herbicide behaviour within the landscapes. In the Morris site 100, 138, and 63 sampling points were allocated to upper, middle, and lower LECs, which encompassed 33%, 46%, and 21% of the 301 points, respectively. At Miniota a total of 51, 72, 73, and 14

sampling points were allocated to the upper, middle, lower, and depressional LECs, which comprised 24%, 34%, 35%, and 7% of the 210 points, respectively.

However, concerns were raised about microbial degradation of the herbicide during the sorption experiments, thus a preliminary study was first conducted to determine the effects of soil sterilization by mercuric chloride on the sorption of the 2,4-D by soil. Results indicated the mercuric chloride strongly decreased the capacity of the soil to retain herbicides and that the interference of the mercuric chloride with herbicide sorption increased with increasing soil organic carbon contents.

At Morris, from the upper to the middle to the lower LECs, the average Ap horizon depth did not significantly increase, but the amount of carbonates decreased, and both soil pH and percent soil organic carbon (%SOC) increased. The herbicide was weakly bound to the soil constituents as its average soil-water partitioning coefficient, ( $K_d$ ) was 0.3 ml/g, its average organic carbon sorption partitioning coefficient ( $K_{oc}$ ) was 24.5 ml/g, and 49.0% of the sorbed herbicide desorbed. The herbicide's  $K_d$  increased significantly from the upper to the middle to the lower LEC. In the upper LEC, significantly lower values for both  $K_{oc}$  and percent herbicide desorption occurred relative to the other LECs.

At Miniota, the average Ah horizon depth, solum depth, and %SOC values were all significantly greater in the depressional LEC compared to the upper, middle, and lower LECs. The average  $K_d$  was 0.6 ml/g, the average  $K_{oc}$  was 24.5 ml/g, and 65.0% of the

sorbed herbicide desorbed. These indicate that the herbicide was weakly bound to the soil particles. The herbicide's  $K_d$  was found to differ with LEC where the lower and depressional LECs sorbed more 2,4-D relative to the upper and middle LECs. Both  $K_{oc}$  and percent herbicide did not significantly differ with landscape position.

The linear correlation between %SOC and the 2,4-D sorption was stronger at Miniota ( $r = 0.71$ ,  $P < 0.01$ ) than at Morris ( $r = 0.23$ ,  $P < 0.01$ ). The Morris' soil pH and carbonates had more of an influence on the herbicide sorption than the soil organic carbon content. The herbicide's  $K_d$  was the best parameter that explained for the Morris herbicide desorption behaviour, while SOC and  $K_d$  were the two parameters that best explained for the variation of the 2,4-D desorption at Miniota.

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## FOREWORD

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## LIST OF ABBREVIATIONS

1. SOC : Soil organic carbon
2. SOM: Soil organic matter
3. LEC: Landform element complex
4. *Ap d*: Depth of A horizon
5. *CO<sub>3</sub> d*: Depth to carbonates
6. *Solum d*: Solum depth
7. 2,4-D: 2,4-Dichlorophenoxyacetic acid
8.  $K_d$ : The soil-water adsorption distribution coefficient
9.  $K_{oc}$ : The organic carbon distribution coefficient

## 1. INTRODUCTION

Almost all of the pesticides manufactured and used today are synthetic organic chemicals, which have replaced inorganic chemicals that were earlier used as a form of pest control. Pesticides have effectively reduced the need for tillage and cultural practices as the means for insect, weed, and disease control in modern agroecosystems (Cheng 1990). Pesticide use has helped to support the vast increases in worldwide agricultural food and fibre production and most likely will continue to facilitate crop production well into the future.

In the Canadian prairie provinces, agriculture is a major industry in which most of the cultivated land in this area is treated with pesticides (Waite et al. 2002). Herbicides are the most often used pesticide in which more than 20 million kg were applied in 1990 on farms in Manitoba, Saskatchewan, and Alberta (Environment Canada, unpublished data, 1991). One extensively used herbicide is 2,4-Dichlorophenoxyacetic acid (2,4-D). For example, in 1990, more than 3.8 million kg of 2,4-D was applied on agricultural land within these Canadian prairie provinces (Waite et al. 2002). In fact, since 2,4-D was discovered as a herbicide during World War II, this synthetic organic chemical evolved into one of the greatest advances in worldwide weed control (Peterson 1967). This herbicide is important for controlling broadleaf weeds, particularly in Western Canada, which has extensive acreages in cereals.

Once introduced into agricultural fields a portion of the applied pesticides leave their target environment and may cause harmful environmental effects (Flury 1996). Pesticides are, by their chemical nature and design, toxic compounds and when present in groundwater could pose a health hazard to both humans and other organisms (Lampman 1995). Recently many concerns have been raised about the potential for pesticides to leach into groundwater under areas of repeated annual pesticide applications (Miller et al. 1995a) and numerous occurrences of pesticide contamination of waterways have been reported in the United States (Mass et al. 1995) and in Canada (McRae 1989). Since over 90% of Canadian pesticide usage is in agricultural areas, where rural people acquire their drinking water from wells (Crowe and Milburn 1995), avoiding groundwater contamination from pesticides in Canada should be of great importance.

Many processes control pesticide movement in the environment, which include sorption onto soil constituents, plant and soil fauna uptake, transformation or degradation processes, and transport losses in liquid or in gaseous form (Ross 1989). Of these processes, sorption and desorption are the most critical as they will affect the pesticides' behaviour by controlling pesticide degradation and transport processes. As such pesticide sorption and desorption processes also determine whether the pesticides become pollutants and harmful to non target organisms and whether they will be efficacious for pest control (Wauchope et al. 2002).

Soil physical and chemical properties will affect the intensity and amount of pesticide sorption and desorption in agricultural fields, where soil organic carbon (SOC) is the best

predictor of sorption for nonpolar, nonionizable organic chemicals (Koskinen and Harper 1990). For polar, ionizable chemicals, additional factors such as clay content and pH could also affect the amount and strength of pesticide sorption (Green and Karickhoff 1990). These soil properties will vary both spatially and temporally (Oliveira Jr. et al. 1999) because of soil formation processes and agricultural management practices. For example, soils at bottom slope positions tend to have greater soil organic matter content than soils in upper or middle slope positions (Mallawatantri and Mulla 1992, Vink and Robert 1992, Khakural et al. 1994, Farenhorst et al. 2001). Land management practices such as intensive tillage usually causes soil loss, in convex upper slope positions, and soil accumulation in concave lower slope landscape positions. Tillage also results in accelerated organic matter decomposition and increased losses of organic matter rich topsoil by wind and water erosion (Bowman et al. 1990, Arshad et al. 1990) relative to zero-tilled fields. As well, soil aggregate stability, aggregate size, pore continuity, and infiltration rates are all decreased by tillage (Carter 1992). With decreased amounts of soil organic matter in heavily-tilled sites, less pesticide sorption onto soil may occur.

Landscape based agricultural management is an emerging technology that allows better matching of inputs to field situations (Larson and Robert 1991). Under this management style, all chemical input applications are optimized according to the local soil and landscape characteristics as to decrease surface and groundwater pollution and to maintain or increase net returns (Khakural et al. 1994). However, few pesticide sorption and no pesticide desorption studies have incorporated landscape spatial variability. Some information exists that in tilled sites with lower SOC contents, less pesticide sorption to

soil occurs, relative to zero-tilled sites. In addition, little is known about the effects that soil surface exposed carbonates in heavily-tilled sites has on pesticide behaviour in soil. This is a concern since in hummocky agricultural sites, with intensive tillage, the carbonate content in surface soils can be high. This is also the soil layer where pesticides are applied.

Therefore, the objective of this study was to quantify and correlate the spatial variability of soil properties and 2,4-D sorption and desorption within two agricultural sites. This study is important for identifying high risk zones within agricultural fields, particularly those that could lead to groundwater contamination by pesticides. Understanding the location of these zones could further lead to the development of alternative pest control measures, including those that have shown to reduce non-point source pollution by pesticides. For example, Khakural et al. (1994) site-specifically applied alachlor to a fine loamy Minnesota soil, which reduced the pesticide's concentrations in surface runoff, which lessened its adverse environmental effects relative to a uniform application rate. As well, this study is further advancing the effect that soil carbonates have on pesticide sorption and desorption behaviour.

Microbial degradation of labile organic compounds in soil sorption studies may lead to erroneous results if a radiolabeled compound and the batch sorption technique are used (Koskinen and Cheng 1982, Scott et al. 1982, Scott et al. 1983). As the amount of  $^{14}\text{C}$  in the equilibration solution is measured, any  $^{14}\text{C}$  labeled degradation product (i.e.  $\text{CO}_2$  or metabolites) in solution would lead to an underestimation of sorption (Wolf et al. 1989).

An overestimation of sorption can occur if any metabolites or degradation products are sorbed or precipitated (Wolf et al. 1989). Thus, this study first determined what effects the soil sterilizer compound, mercuric chloride, has on the sorption of the 2,4-D in soil.

## **2. LITERATURE REVIEW**

### **2.1 The spatial variability of soil properties**

#### **2.1.1 Solum development**

Soils are formed and influenced by five factors: climate, parent material, topography, organisms, and time (Jenny 1941). Soils develop through progressive and regressive pedogenesis. Progressive pedogenesis includes the processes of horizonation, developmental upbuilding, and soil deepening where regressive pedogenesis includes the loss of definition between soil horizons and soil removal (Manning 1999). In essence, soil formation involves additions and losses to soil, translocations within the soil, and transformations of material within the soil (Greenland and Hayes 1981). Although soils are constantly developing, significant spatial variability in soil properties can occur over relatively small distances within landscapes because of these progressive and regressive soil formation processes.

Depth to carbonates and A horizon depth are both key indicators of progressive soil development of Chernozemic soils in glacial-depositional parent material (Manning 1999). The A horizon is formed in regions where materials in solution or suspension are leached, and/or where maximum in situ accumulation of organic matter occurs (Agriculture Canada Expert Committee on Soil Survey 1987). The addition of organic matter results in the darkening of the surface soil to produce an Ah horizon. However,

when organic matter is removed, it is expressed by a lightening of the soil colour to produce an Ae horizon (Agriculture Canada Expert Committee on Soil Survey 1987).

Landscape morphology along with soil pedogenesis processes will also result in spatial distributions of soil properties. For example, Pennock et al. (1987) determined that the thickness of A horizons and the depths to calcium carbonates in Saskatchewan landscapes were steadily greater in convergent (i.e. points where water comes together from different directions) versus divergent elements (i.e. points where water starts to flow in different directions) within a given landscape. More importantly A horizon depth and depth to carbonates increased from shoulders to backslopes to footslopes landscape positions (Pennock et al. 1987). Other researchers have observed thin soils with low productivity and low leaching potential on upper convex slopes as a result of erosion, whereas deeper soils in lower slopes had greater fertility and more intense leaching regimes, with enhanced deposition of eroded sediments (Anderson 1987, Miller et al. 1988, Moulin et al. 1994, Simmons et al. 1989, Fiez et al. 1994).

Different soil series within landscapes will also emerge due to the spatial variability of the soil properties. For example, King et al. (1983) in Saskatchewan determined that thin Calcareous or Regosol Chernozemic soils with thin or non-existent B horizons were situated in convex upper slopes. Midslope positions had Orthic Chernozems but the concave lower slope and depressional areas were dominated by Eluviated or Gleyed soils with agrillic B horizons (King et al. 1983).

In addition to water and wind erosion, tillage erosion will also influence the A horizon depth. Under similar gradients, the thickness of the A horizon is less under cultivation than under native grasses, while in the depositional regions of the landscape, the thickness of the A horizon is greater under tillage than under native grasses (Mermut et al. 1983). Tillage action causes for soil on upper slopes to be eroded and deposited onto the depressional regions, thus increasing the depressional regions' A horizon depth .

Pesticide behaviour in soil is influenced by many soil characteristics including pH and soil organic matter content (Novak et al. 1997, Oliveira Jr et al. 1999, Farenhorst et al. 2001). However, little is known about the influence that carbonates have on pesticide sorption. These three soil properties spatially vary within landscapes due to soil formation processes. Therefore, to further understand the spatial variability of pesticide behaviour across landscapes, it is then important to review the characteristics of soil carbonate content, soil pH, and soil organic matter content.

### **2.1.2 Carbonates**

Soil inorganic carbon occurs usually as calcite ( $\text{CaCO}_3$ ), dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ], and magnesian calcite ( $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$ ) (Goh et al. 1993). Since these minerals are alkaline, they act as soil pH buffers (Loeppert and Suarez 1996).

The location and dispersal of carbonates in soils are influenced largely by climate (Doner and Lynn 1989). If other soil forming factors are held equal, an increase in rainfall will increase the leaching of carbonates from the upper soil surfaces to deeper layers where

they will be deposited (Doner and Lynn 1989). Carbonates are relatively soluble in soil water and can be easily redistributed within the soil (FitzPatrick 1980), either vertically or laterally depending on texture and slope (Doner and Lynn 1989). For example, Knuteson et al. (1989) attributed high carbonate content in rego soils, located on slightly sloping planar slopes beside depressional areas, to upward fluxes of carbonates as a result of water movement from the water table to the surface. Moulin et al. (1994) reported “rego rings” near recharge depressions where upward water flux had resulted in carbonate-rich surface soils in central Saskatchewan. High calcium carbonate levels were also present in the knoll positions where the subsoil material had been exposed by erosion and tillage. Brubaker et al. (1993), who focused on Nebraska silt loam and silty clay soils, reported that  $\text{CaCO}_3$  generally increased downslope and with depth. These differences were attributed to soil formation and soil erosion processes (Brubaker et al 1993).

### **2.1.3 Soil pH**

In the glacial depositional surface soils of the Prairie Ecozone of Western Canada, alkaline pH values predominate (Manning 1999). An alkaline soil pH occurs where large amounts of calcium and magnesium carbonates are present (Manning 1999). Soil acidic values are derived mainly from the presence of hydrogen and aluminum ions (Fitzpatrick 1980). In an Oxbow catena in southern Saskatchewan, Spratt and McIver (1972) reported pH values to be mostly alkaline varying from 7.8 in the upper slopes and decreasing to 7.4 in the depressions. In eastern Nebraska silt loam and silty clay soils, Brubaker et al. (1993) observed that pH somewhat increased downslope and with depth,

which was attributed to increases in carbonates and to the local site use of anhydrous  $\text{NH}_3$  fertilizer. Mallawatantri and Mulla (1992), in a Washington state study, found the mean soils' pH decreased significantly from upper (7.12) to lower (5.42) slope landscape positions. At these upper slope positions, the neutral soil pH was possibly due to the exposure of subsoil material that was less acidic than the surface soil. The acidic pH values at the mid and lower slope locations resulted from long term fertilizer applications (Mallawatantri and Mulla 1992).

#### **2.1.4 Soil organic matter**

Soil organic matter (SOM) originates from plant residues, compost, and in some cases from animal manures and sewage sludge applications (Paustian et al. 1997, Collins et al. 1997). SOM is formed through many complex processes involving: (1) decomposition of the residues into simple carbon compounds; (2) the assimilation and repeated cycling of carbon through the microbial biomass with the formation of new microbial cells; and (3) microbially mediated polymerization of organic compounds (quinones) occurs and lignins are modified in which high-molecular weight, brown to black colored polymers are formed (Figure 2.1, Collins et al. 1997, Stevenson 1972).

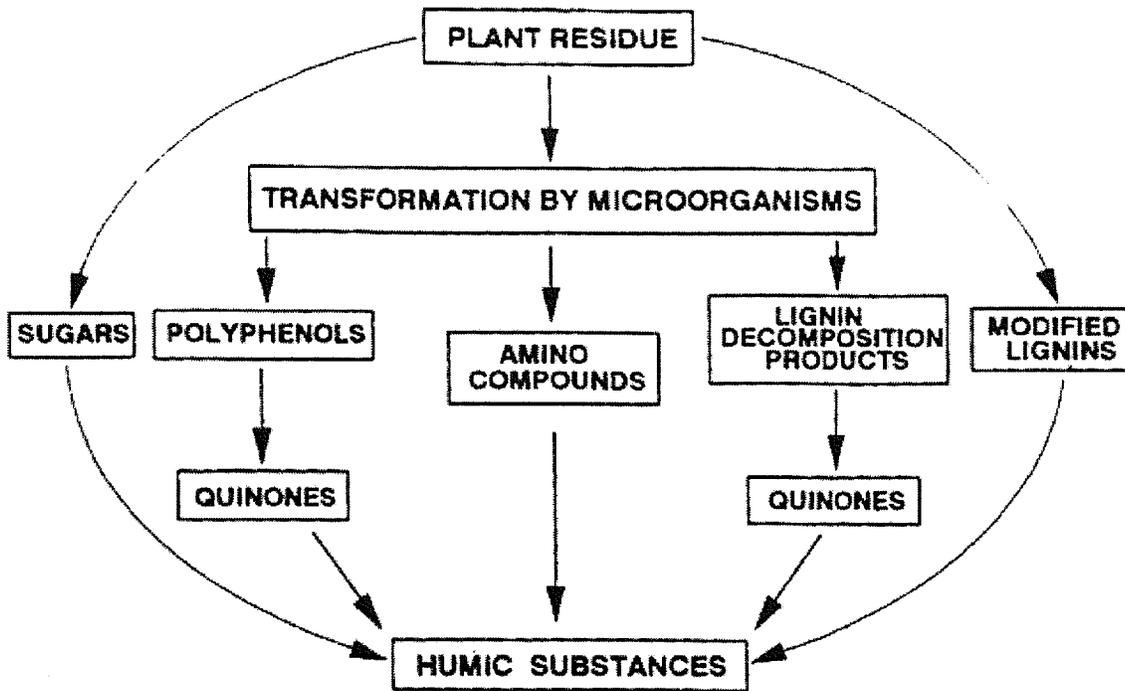


Figure 2.1 The transformation processes involved during the formation of humic substances (Collins et al. 1997).

The types and amounts of organic matter in soil are controlled by the difference between the inputs of organic matter and outputs through nutrient mineralization, soil erosion, and nutrient leaching (Paustian et al. 1997). Decomposed organic matter can be classified into one of three major fractions: humic acids, fulvic acids, and humin, based on their solubilities in alkaline and acid solutions and on their chemical properties (Figure 2.2, Collins et al. 1997, Stevenson 1972).

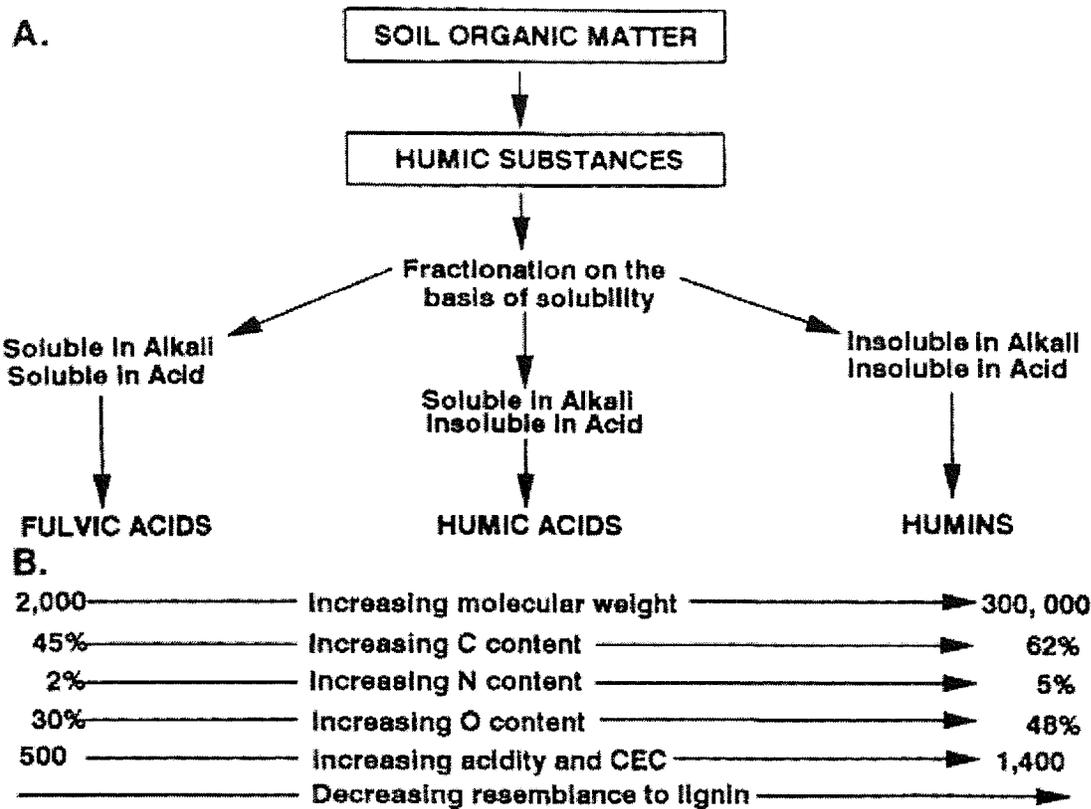


Figure 2.2. (a) The classical fractionation of SOM and (b) characteristic properties of humic substances (Collins et al. 1997).

The content and nature of SOM plays a major role in determining the fate of organic chemicals, including pesticides (Stevenson 1972, Senesi 1992). Of the three humic substances, the humic acid fractions have the greatest effect on the capacity of a soil to sorb organic chemicals (Clapp et al. 2001, Senesi et al. 2001). The ability of humic acids to bind with organic chemicals is mainly because they have a high content of oxygen containing functional groups which include phenolic, aliphatic and enolic-OH, and C=O structures of many sorts (Stevenson 1972).

Usually, the amount of soil organic carbon (SOC) within soil organic matter is considered to be around 58% in which the organic matter content can be estimated by multiplying the percentage of organic carbon by 1.724 (Foth 1978). Soil organic carbon influences soil structural stability, water holding capacity, nutrient bioavailability, buffering capacity, and soil biodiversity (Bajracharya et al. 1997). Therefore, SOC controls and regulates several soil processes related with soil degradation and productivity (Bajracharya et al. 1997). SOC is positively correlated with topsoil depth, available water hold capacity (Gollany et al. 1992), and total nitrogen (Gregorich and Anderson 1985). Losses of carbon occur through the decomposition and mineralization of organic compounds by soil microorganisms with carbon dioxide being the dominant product (Paustian et al. 1997). As well, organic compounds may be leached from the soil profile as dissolved organic compounds (Paustian et al. 1997).

Various studies have demonstrated that the distribution of SOC within agricultural landscapes is not arbitrary. Generally, surface soil samples have overall lower concentrations and amounts of SOC at divergent upper slope positions relative to depositional and convergent lower slope positions (Manning 1999). Miller et al. (1988), Mallawatantri and Mulla (1992), Novak (1999), and Farenhorst et al. (2001) have all reported that soil organic carbon contents were greater in bottom slope positions than in upper slope positions in agricultural fields. Malo et al. (1974) measured % SOM in the A horizon and found that slope positions with larger erosion rates showed lower SOM than slope positions with smaller erosion rates. Upper slope positions often have greater

erosion rates and less topsoil, than at bottom slope positions (Fitzpatrick 1980). Eroded material from upper slope positions is often deposited downslope (Novak 1999).

Cultivation greatly alters the amounts and quality of SOM within agricultural landscapes. Many studies have reported greater amounts of SOC under reduced or zero-tillage compared with soil under tillage, and differences in SOC between tillage systems are largest for surface soils (Havlin et al. 1990, Doran 1987, Franzluebbers et al. 1995, Salinas-Garcia et al. 1997, Novak 1999). Intensive tillage results in fewer amounts of crop residues being returned to the soil surface, accelerated organic matter decomposition, and losses of organic matter rich topsoil by wind and water erosion (Bowman et al. 1990, Arshad et al. 1990). SOC concentrations in the plow layer (0-15 cm) could decrease quickly and continuously for several years after cultivation but SOC amounts do eventually stabilize (Paustian et al. 1997). For a Colorado sandy loam that had been cultivated for 60 years, Bowman et al. (1990) determined that the total SOC in the 0-15 cm soil layer had decreased by 62% and the labile organic carbon fraction had declined by 72%, when compared to an adjacent virgin rangeland site. More than over half of these carbon losses had occurred during the first 3 years of cultivation (Bowman et al. 1990). In British Columbia, Arshad et al. (1990) concluded that tillage had a negative effect on the quality of SOM when compared to SOM in zero tilled field. The zero tilled soil had a greater content of carbon and nitrogen, carbohydrates, amino acids, aliphatic carbon (paraffins) and had less aromatic carbon than the conventionally tilled soil.

## 2.2 The herbicide 2,4-Dichlorophenoxyacetic acid

### 2.2.1 History and usage

The chlorinated phenoxy herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) (Figure 2.3) was first patented for use as a plant growth regulator compound in 1943 (Peterson 1967), making it the first successful selective, systemic herbicide ever developed (Industry Task Force II On 2,4-D Research Data 2001). Three years later, 2,4-D was registered for use as a herbicide in Canada (Anonymous 1994).

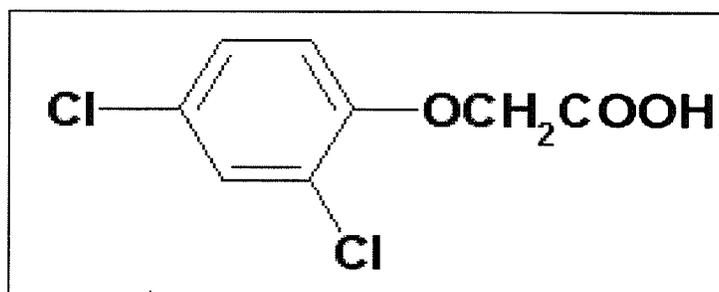


Figure 2.3 The chemical structure of 2,4-D.

The chemical 2,4-D is a post emergent herbicide used to control many broadleaf weeds (Table 2.1) in agricultural fields (i.e. cereals and field corn), roadsides, forests, household lawns, and on golf courses. The herbicide mimics the plant hormone auxin (National Pesticide Information Centre 2003) and is absorbed through the plants' foliage and roots where it is translocated to actively growing parts (Manitoba Agriculture and Food 2000). The herbicide acts as a poison by causing quick plant cell division and abnormal growth (National Pesticide Information Centre 2003). Plants that have been sprayed by 2,4-D will show bending and twisting of leaves and stems within 2 to 7 days, followed by

browning and death 3 to 4 weeks after application (Manitoba Agriculture and Food 2000).

Table 2.1 Common weeds controlled by 2,4-D (Manitoba Agriculture and Food 2000).

<b>Weeds:</b>	
Canada thistle ( <i>Cirsium arvense</i> )	Redroot pigweed ( <i>Amaranthus retroflexus</i> )
Common lamb's-quarters ( <i>Chenopodium album</i> )	Russian thistle ( <i>Sasola iberica</i> )
Dandelion ( <i>Taraxacum officinale</i> )	Shepherd's purse ( <i>Capsella bursa-pastoris</i> )
Kochia ( <i>Kochia scoparia</i> )	Sow thistle ( <i>Sonchus arvensis</i> )
Leafy spurge ( <i>Euphorbia esula</i> )	Stink weed ( <i>Datura stramonium</i> )
Ragweed ( <i>Ambrosia artemisiifolia</i> )	Wild mustard ( <i>Brassica kaber</i> )

The herbicide is very popular among agricultural producers. In fact, 2,4-D is the most widely used agricultural herbicide worldwide (Industry Task Force II on 2,4-D Research Data 2001, National Pesticide Information Centre 2003). Being used for more than 50 years, 2,4-D is currently the third most widely used herbicide in Canada and in the United States (Industry Task Force II on 2,4-D 2001). In 1990, Canadian prairie farmers used over 3.8 million kg of 2,4-D (Waite et al. 2002), which was roughly 19% of total herbicide usage in western Canada (Waite 2001 person. comm). An earlier report indicated that in southern Manitoba alone, during the late 1980s, an estimated half a million kg per year of 2,4-D was used (Rawn et al. 1999a).

### 2.2.2 The herbicide 2,4-D in the environment

In agriculture, 2,4-D is applied by tractor-drawn delivery systems as either an amine salt or as a low-volatile ester (Waite et al. 2002). Following application, the fate of the herbicide is governed by its chemical properties (Table 2.2) and through soil retention, transformation, and transport mechanisms in soils (Figure 2.4, Cheng 1990, Farenhorst et al. 2001). Retention or sorption is the soil's ability to retain a pesticide molecule, thus preventing it from moving either within or outside the soil matrix (Koskinen and Harper 1990). Pesticide transformation is where the parent molecule is altered either through biotic or abiotic processes (Koskinen and Harper 1990). Pesticide transport mechanisms include: pesticide volatilization into the atmosphere, which is controlled by the pesticide's vapour pressure, and pesticide movement into surface or groundwater, which is controlled by the pesticide's soil-water partitioning coefficient ( $K_d$ ), the organic carbon sorption partitioning coefficient ( $K_{oc}$ ), and the pesticide's water solubility (Cheng 1990). Therefore, sorption affects the availability of the pesticide for transformation and transport processes and for uptake by plants and by soil fauna (Cheng 1990, Farenhorst et al. 2001, Koskinen and Harper 1990).

Table 2.2 The chemical properties of 2,4-D

Chemical Properties					
	Water solubility	Vapour pressure	Acid $pK_a$	Soil half life	$K_{ow}$ (c)
Values	860 mg/l (a)	$8 \times 10^{-6}$ mmHg (a)	2.64-2.87 (b)	10 days (a)	2.81 (a)

a is from the British Crop Protection Council (1987)

b is from Clausen et al. (2001)

c is the pesticide's octanol-water partitioning coefficient

Since 2,4-D has a low sorption capacity to soil particles, a moderate water solubility, and a moderate vapour pressure, the potential for herbicide movement outside the soil matrix exists. This may include the movement of 2,4-D to non-target environments where the herbicide will then act as a pollutant.

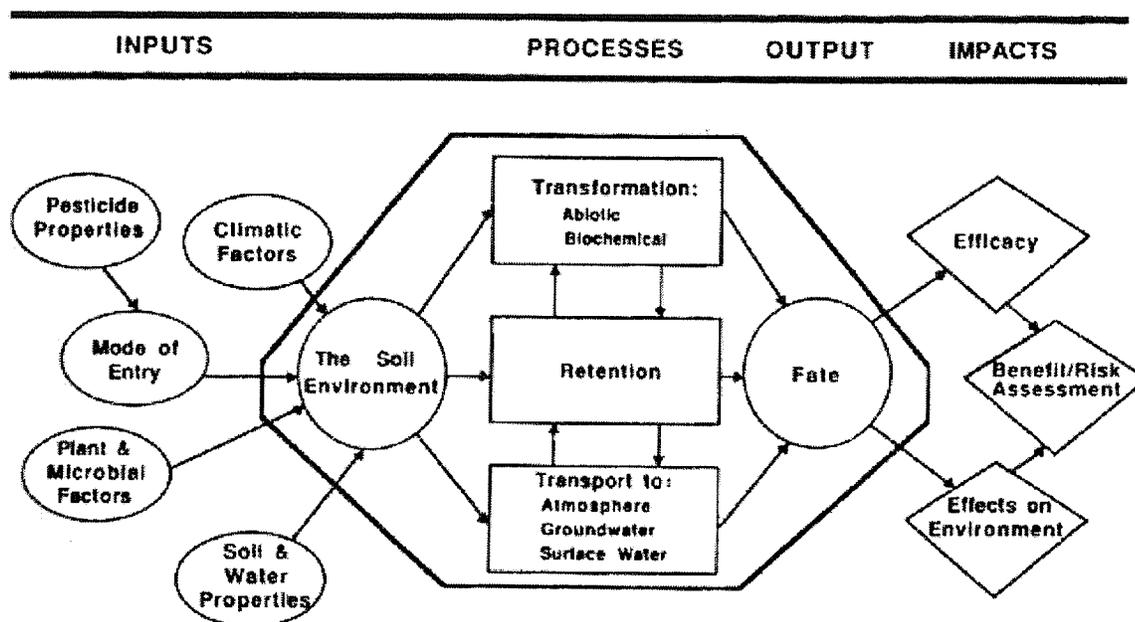


Figure 2.4 A conceptual diagram illustrating the factors and processes that affect the fate of pesticides in the soil environment and how pesticides fate affects the efficacy and their impact on the environment (Cheng 1990).

The herbicide 2,4-D has been detected in surface and groundwater sources in agricultural areas but at low concentrations (Table 2.3). In a 1979-1984 Ontario rural well study, 2,4-D was one of the major pesticides found (Frank et al. 1987). The authors noted that this contamination derived mostly from spills, spray drift, back-siphoning, and surface runoff. However, the chance that a few of the detected pesticides had leached through the soil in

treated fields and entered the wells (groundwater) was not eliminated (Frank et al. 1987).

Miller et al. (1995b) reported that 2,4-D was detected 48% of the time in Alberta

Table 2.3 Locations and amounts of where 2,4-D has been detected in some Canadian Prairie waterways

a. Groundwater quality studies

Location	Year	Herbicide concentrations [ ug L <sup>-1</sup> ]	% of samples with 2,4-D of (total samples)	Reference
Near Regina, SK.	1985-87	0.34 (mean)	10 (105)	Waite et al. (1992)
Taber, AB.	1991	1.8 (mean)	48 (56)	Miller et al. (1995b)

b. Surface water quality studies

Location	Year	Herbicide concentrations [ ug L <sup>-1</sup> ]	% of samples with 2,4-D of (total samples)	Reference
LaSalle River, MB.	N/A	<.010 to .130	N/A	Williamson (1984)
Ochre and Turtle Rivers, MB.	1984	0.0023-0.83 (Mean monthly values)	N/A	Muir and Grift (1987)
Near Regina, SK.	1985-87	0.11 (mean)	34 (64)	Waite et al. (1992)
Dugouts in SK	1987-89	0.08 (median)	81(191)	Grover et al. (1997)
10 Permanent Lakes in SK	1988	0.071 (mean)	N/A	Donald and Syrgiannis (1995)
9 Semi-permanent lakes in SK	1988	0.1168 (mean)	N/A	Donald and Syrgiannis (1995)
South Tobacco Creek, MB.	1993-96	<0.00001-.680	N/A	Rawn et al. (1999a)

N/A = Not available

groundwater samples, in which its average concentration was 1.8 ug/L. Currie and Williamson (1995) examined several southern Manitoba river waters for some 65 pesticides and found 2,4-D to be the most frequently detected herbicide. However, in only 0.1% of the samples did the detected 2,4-D exceed its aquatic water quality guideline of 4 ug/L (Currie and Williamson 1995).

Rawn et al. (1999a) detected 2,4-D in creek water samples within the Manitoba South Tobacco Watershed in concentrations varying from less than 0.011 ng/L to 680 ng/L. Elevated 2,4-D concentrations reflected local application times in this four year water quality study. In the Red River at Emerson MB, the maximum 2,4-D seasonal concentrations happened in June that corresponded to peak 2,4-D applications in North Dakota, which is upstream from Emerson (Tornes and Brigham 1994).

In atmospheric samples, 2,4-D has also been detected and this contamination has been related to local application use. For example, during a four year period, 2,4-D was detected in 67% of air samples taken near Regina, SK. in which its seasonal concentration in air varied from 38, 600 to 137,400 ng/m<sup>2</sup> (Waite et al. 1995). The maximum amounts of 2,4-D atmospheric deposits occurred during the local application times, which was then followed by quick declines (Waite et al. 1995). In the Manitoba South Tobacco Creek Watershed area, 2,4-D was present in air samples in concentrations as high as 3.5 ng/m<sup>3</sup> (Rawn et al. 1999b). Although this was much lower than the concentrations found in Saskatchewan by Waite et al. (1995), the herbicide was present in both air and precipitation samples, and the maximum concentrations reflected times of

local use (Rawn et al. 1999b). In North Dakota, Hawthorne et al. (1996), reported seasonal maximum air concentrations of 2,4-D levels as high as  $1.8 \text{ ng/m}^3$ . Muir and Grift (1995) detected 2,4-D in a lake in the Ontario Experimental Lakes Area where atmospheric sources were the only contributor and is an area a long distance from any potential sources.

The herbicide 2,4-D is mobile in soil, due to its low adsorptive capacities but its ability to leach is reduced due to its relatively quick degradation and mineralization rates (Ou et al. 1978, Parker and Doxtader 1982). Research has shown that 2,4-D can degrade quickly, because the herbicide can either be co-metabolized or used as a carbon and energy source by soil microorganisms (Fournier 1980). During the crop growing season, 2,4-D in soil, under optimal soil conditions, is broken down within 4 to 6 weeks of application (Gold et al. 1988) in which its field half-life is 10 days (Waite et al. 2002).

Willems et al. (1996) reported that 2,4-D mineralization rates in a sandy loam soil were on average 4 times greater at depths between 1 and 1.5m than at the soil surface layer. One possible explanation for this is that, in the soil surface, a considerable amount of readily available soil organic carbon exists, which microbes might prefer to use instead of 2,4-D (Willems et al. 1996). At lower depths in the soil profile, microbial activity is reduced because of low amounts of available energy and organic carbon and, as such, the presence of 2,4-D would be readily used as an energy source by microorganisms, therefore giving greater 2,4-D mineralization rates relative to surface soils (Willems et al. 1996). These observations show that 2,4-D mineralization can occur at all soil depths

and needs to be considered when examining 2,4-D leaching potential to groundwater (Willems et al. 1996).

### **2.3 Sorption Mechanisms of 2,4-D**

The adsorption of chemicals occurs when the solutes in a solution are fixed upon the surface of a solid whereas absorption is when the chemical molecules in a solution are taken up within the mass of adsorbing phase (Morrill et al. 1982). In practice, adsorption is usually replaced by the more common term sorption, which refers to a general retention process that has no distinction between the specific processes of adsorption and absorption (Koskinen and Harper 1990). Sorption is also a reversible process comprised of the attraction of a chemical to the soil particle surface and the retention of that chemical on the surface for a time that depends on the affinity of the chemical for the surface (Koskinen and Harper 1990). The chemical composition of the media surrounding the soil particle surface may influence the sorption process. The extent and amount to which pesticides are sorbed and desorbed in soil, are determined by two major factors: (1) the chemical nature of the pesticides and (2) the physical and chemical properties of the soil (Stevenson 1972).

The herbicide 2,4-D can be sorbed onto SOM by at least 3 bonding mechanisms: (1) London van der Waals forces, (2) Hydrogen bonding, and (3) hydrophobic sorption or partitioning. When sorbed, a pesticide may be easily desorbed, desorbed at different rates or permanently sorbed (Senesi 1992) depending on the strength of the sorption bonds.

### **2.3.1 London–van der Waals forces**

London-van der Waals forces are comprised of weak, short-range dipolar or induced dipolar attractions that function, with other binding forces, in all adsorbed-adsorbate interactions. These interactions occur when the electric motion in each of two adjacent molecules is mutually correlated to make a tiny net electrostatic attraction at all times (Koskinen and Harper 1990). Since London-van der Waals forces are additive, their role increases with the size of the interacting molecules (Senesi 1992). These forces are important for the sorption of nonionic and ionizable pesticides on suitable sites of humic acid molecules and are believed to be involved in the sorption onto soil of carbaryl, parathion, alachlor, cycloate, benzonitrile, DDT, picloram, 2,4-D, several thiocarbamates, carbothioates, and acetanilides onto soil (Senesi 1992).

### **2.3.2 Hydrogen bonding**

Hydrogen bonding has stronger dipole-dipole interactions than the London-van der Waals interactions and is produced from the electrostatic attraction between an electropositive H nucleus and the exposed electron pairs on electronegative atoms (Koskinen and Harper 1990). Hydrogen bonding may occur on clay surfaces, connecting a pesticide with the clay surface oxygen atoms or to protons of the adsorbed water (Morrill et al. 1982). Organic compounds with carbonyl groups are also adsorbed on clay because of the H-bonding between the double-bonded oxygen of the carbonyl group and a H-atom of the clay lattice (Morrill et al. 1982). Hayes (1970) stated that H bonding is important in the sorption of triazines. Weakly-acidic and anionic pesticides such as chlorophenoxyalkanoic acids, including 2,4-D, esters, asulam, and dicamba, can also be

adsorbed by H-bonding onto humic substances particularly at pH values below their  $pK_a$  as the weakly-acidic pesticides are then mostly in the non-ionized form and may sorb through their COOH, COOR, and similar groups (Senesi 1992).

### **2.3.3 Hydrophobic sorption and partitioning**

This sorption mechanism is proposed as a pH-independent mechanism for the retention of many pesticides, including 2,4-D, by the hydrophobic active sites of humic substances that interact weakly with water (Senesi 1992). These sites include aliphatic side chains or lipid portions and lignin derived moieties with a high carbon content and a small number of polar groups of the humic macromolecule substances (Senesi 1992).

### **2.3.4 The Freundlich isotherm**

The amount that pesticides adsorb to soil will depend on the number of sorption sites and is often a function of specific surface and charge density of soil particles (Morrill et al. 1982). Sorption isotherms are obtained by measuring the amount of solute adsorbed at a constant temperature for a variety of concentrations and are usually described by the Freundlich equation (Morrill et al. 1982).

The Freundlich isotherm is a non-saturable sorption event since there is the potential for forming various layers as the bonding is not a direct chemical bond but rather involves a lower energy physical association. The equation for this isotherm is :  $S = K_f C^{\frac{1}{n}}$  [1]

where  $S$  is the amount of pesticide sorbed (mg/g) and  $C$  is the solution concentration of

the pesticide (mg/mL) (Reddy et al. 1997a). The Freundlich coefficient ( $K_f$ ) and the Freundlich exponent ( $n$ ) are empirical constants (Reddy et al. 1997a) that describe the curvature of the isotherm. When  $n = 1$ , a linear isotherm exists which approximates a partitioning phenomena where the affinity of the pesticide is independent of the concentration over a wide range of values. In this case, the Freundlich  $K_f$  is equivalent to the soil-water partitioning coefficient,  $K_d$ .

In terms of 2,4-D's sorption isotherm shape, many authors have reported that it fits well to the Freundlich type isotherm (Grover 1973, Khan 1973, Rao and Davidson 1979, Susarla et al. 1993, Cheah et al. 1997, Sannino et al. 1997).

### **2.3.5 Studies of 2,4-D sorption onto soil constituents**

Khan (1973) examined the equilibrium and kinetic sorption of 2,4-D onto humic acids in a Black Chernozemic soil of western Canada. This study reported that the rate-limiting step for the initial sorption period was the diffusion of the herbicide molecules to the humic acid's surface. At longer time intervals, the rate-limiting step was the intraparticle diffusion of the herbicide molecules into the humic acid particles' interiors (Khan 1973). These findings fit with the notion that the humic acid structure is loose or open (Orlov and Gleborva 1972). Grover (1973) determined that the sorptive behaviour of the acid and ester forms of 2,4-D were similar in seven Canadian prairie soils and 2,4-D acid sorption was well correlated ( $r = 0.86$ ) with soil organic matter but not with the amount of clay ( $r = 0.26$ ).

Soil organic carbon content is positively correlated with 2,4-D sorption by soil. Both Mallawatantri and Mulla (1992) and Farenhorst et al. (2001) found that 2,4-D sorption by soil was significantly greater in lower landscape positions than in upper slope positions, which was reflective of the differences in SOC distribution within the landscapes. Mallawatantri and Mulla (1992) also found that 2,4-D sorption was significantly greater for soils from a low chemical input farm than soils from a conventional farm for any given slope position. Farenhorst et al. (2001) reported that 2,4-D sorption by soil was on average slightly greater on a zero-tilled field than on an adjacent conventionally tilled field, however the prediction of herbicide sorption by soil properties was better for the tilled ( $r = 0.94$ ) than for the zero-tilled field ( $r = 0.73$ ). This occurred because the conventionally tilled field had a wider range of soil organic matter contents than in the zero-tilled field, leading to more spatial differences in herbicide sorption (Farenhorst et al. 2001).

Sannino et al. (1997) studied the sorption of 2,4-D onto hydroxy aluminium montmorillonite complexes. At pH 5 to 6 and in acetate buffer, 2,4-D was negatively sorbed (i.e. was repelled) by pure montmorillonite but the herbicide sorption occurred and increased with increased amounts of  $\text{Al}(\text{OH})_x$  species loaded on the montmorillonite surfaces. The authors stated that both electrostatic interactions between the negative  $\text{COO}^-$  moieties of 2,4-D and the positive sites on clays, as well as ligand exchanges of  $\text{COO}^-$  groups with  $-\text{OH}$  or water at the clay surface were most likely involved in the 2,4-D sorption process.

Hermosin and Cornejo (1991) studied 2,4-D sorption by soil in a variety of 22 Spanish soils. For soils with a low free iron mineral content (<5 %) and phyllosilicates, organic matter was not strongly related to 2,4-D sorption ( $r = 0.20$ ). Rather, the herbicide sorption was influenced by sand ( $r = 0.62$ ), free iron contents ( $r = 0.56$ ), clay ( $r = -0.73$ ), and calcium ( $r = -0.73$ ). For soils with a greater iron content (>5%), SOM had the best relationship with 2,4-D sorption ( $r = 0.86$ ). The reported negative influence of pH and calcium on 2,4-D sorption showed that 2,4-D sorption occurs preferentially when in molecular form whereas the anionic form of 2,4-D had little affinity for soils with a high content of phyllosilicates and negative charges.

Watson et al. (1973) determined that the 2,4-D anion was sorbed reversibly on positively charged goethite surfaces where maximum sorption occurred near the herbicide's  $pK_a$ . They postulated that the sorbed 2,4-D anion molecules were aligned with their hydrophobic aromatic ends pointed towards the solution, while the carboxyl groups were weakly bound to the positive sides of the goethite surface.

## **2.4 Pesticides' desorption behaviour**

Quantifying pesticide desorption will determine whether the pesticide sorption onto soil constituents was a temporary reservoir or was a permanent sink for the compound (Graham-Bryce 1981). Several pesticides have been reported to desorb from soil particles including dicamba (Murray and Hall 1989), atrazine and cyanazine (Clay et al. 1988), sulfentrazone (Reddy and Locke 1998), imidacloprid (Cox et al. 1998), and

imazaquin and imazethapyr (Che et al. 1992). However, pesticides' desorption from soil is not always reversible (Savage and Wauchope 1974, Koskinen et al. 1979, Calvet 1980). The difference between the sorption and desorption isotherms has been related to hysteresis by several researchers including Clay et al. (1988) and Reddy and Locke (1998). A simple sorption-desorption experiment will exhibit hysteresis effects if the relative slowness of the desorption process is not recognized and the same equilibration times are used for desorption (Wauchope et al. 2002). Hysteresis may result from experimental errors or from difficulties including the nonattainment of equilibrium during desorption, formation of precipitates, or loss of the compound due to volatilization, and/or degradation (Koskinen et al. 1979, Calvet 1980). As well, colloidal organic matter present in solution or released from soil may sorb the pesticide or compete with it for sorption sites, or act as a non-centrifugeable sorbent (Wauchope et al. 2002).

Clear evidence exists that 2,4-D can be desorbed into the soil solution after being sorbed. Susarla et al. (1993) determined that 2,4-D desorption was characterized by a non-linear Freundlich isotherm which was different from the corresponding sorption isotherm, but the herbicide's desorption diffusion coefficient was of the same order as the sorption isotherm. Sannino et al. (1997) determined that about 30-40% of the sorbed 2,4-D, was easily desorbed from pure montmorillonite and synthetic chlorite-like complexes. However, despite repeated washings with 0.01M CaCl<sub>2</sub>, the remaining 60-70% of the sorbed 2,4-D was not removed. The authors speculated that the physically adsorbed herbicide molecules would be easily removed from clay particles whereas those linked via the COO<sup>-</sup> groups would be more strongly retained on the clay surface. Cheah et al.

(1997) determined that just over 20% of the sorbed 2,4-D in Malaysian soils was desorbed following four washings with  $\text{CaCl}_2$  solutions. Mallawatantri et al. (1996) observed that the amount of 2,4-D desorption in a silt loam decreased in the order of  $A > \text{Bt-M} = E > \text{Bt}$  horizons but the difficulty of desorbing the 2,4-D from the soil materials also decreased in the order of  $A > \text{Bt-M} = E > \text{Bt}$ . The hysteresis effect was greatest in the E, Bt, and Bt-M materials that were lacking in organic carbon but had a greater clay content than the A horizon (Mallawatantri et al. 1996). Sorption mechanisms such as multilayer sorption onto clays may have been the reason for this hysteresis effect. Watson et al. (1973) found that little hysteresis occurred when 2,4-D desorbed from goethite. The authors attributed that the hysteresis may have been from accumulation of errors during the experiment. Mallawatantri et al. (1996) also reported that as SOC and clay content increased, and as soil pH decreased, the amount of 2,4-D desorption decreased.

## **2.5 Sorption of other pesticides onto soil constituents**

The spatial distribution of pesticide sorption within landscapes has only been studied for a few pesticides. This information is needed to better understand the environmental fate of pesticides. Novak et al. (1997) examined an agricultural Iowa landscape and found that atrazine sorption by soil increased in the order of upland shoulders < level < foot and back slopes < depressional areas. This observation was positively correlated to the field's variations in SOC, pH, and clay content (Novak et al. 1997).

Oliveira Jr. et al. (1999) studied the spatial variability of the imazethapyr sorption onto soil in a predominately loamy Minnesota landscape. The imazethapyr sorption to soil was mostly influenced by soil pH, but under acidic conditions, SOC did have some effect. Detailed analysis of the  $K_d$  variability showed that the landscape could be split into two potential management areas: areas with soil pH > 6.25 and  $K_d < 1.5$  and regions with pH < 6.25 and  $K_d > 1.5$ . This separation allowed Oliveira Jr. et al. (1999) a unique opportunity to classify zones in the field where imazethapyr sorption would be minimal and where there is a greater potential for leaching losses.

Mallawatantri and Mulla (1992, in Washington State, studied how soil properties controlled the sorption of metribuzin, diuron, and triallate at different topographic positions in both a conventionally operated field and in an adjacent low input field. Significant decreases in herbicide sorption were observed at upper slope locations relative to bottom slope positions, reflecting the lower SOC content in the upper slope positions. Herbicide sorption  $K_d$  values were all positively correlated with SOC (Mallawatantri and Mulla 1992).

### **3. EFFECT OF SOIL STERILIZATION BY MERCURIC CHLORIDE ON HERBICIDE SORPTION BY SOIL**

#### **3.1 Abstract**

Microbial inhibitors such as mercuric chloride are frequently used to sterilize soil or soil-water slurries in experimental studies on the fate of xenobiotics in the environment. This study examined the influence of mercuric chloride additions to soil-water slurries on the sorptive behaviour of a phenoxy herbicide (2,4-Dichlorophenoxyacetic acid) in soil. The results demonstrated that mercuric chloride strongly decreased the capacity of the soil to retain herbicides, and that the interference of the mercuric chloride with herbicide sorption increased with increasing soil organic carbon contents. Because of the competitive sorption between mercuric chloride and the phenoxy herbicide, mercuric chloride may not be a good soil sterilization procedure for use in xenobiotic fate studies.

#### **3.2 Introduction**

Various soil sterilization procedures have been used in studies on the fate of xenobiotics in soil and aquatic environments, including the addition of microbial inhibitors such as sodium azide and mercuric chloride to sterilize soil or soil-water slurries (de Jonge et al. 1997, Guthrie and Pfaender 1998, Tsao et al. 1998). Wolf et al. (1989) concluded that mercuric chloride additions to soil was the most effective soil sterilization method as it caused minimal changes in soil properties, relative to eight other techniques.

Microbial inhibitors such as mercuric chloride ( $\text{HgCl}_2^-$ ) can be used for distinguishing the fate of pesticides in sterile and nonsterile environments, thereby giving an understanding of the relative importance of the abiotic and biotic pesticide transformation processes (Bailey et al. 1983, Wang et al. 1989). Mercuric chloride can also be used in batch-equilibrium sorption experiments to prevent microbial degradation of a radiolabeled pesticide during the equilibrium period, thereby improving soil-water partitioning coefficient ( $K_d$ ) determinations (Wolf et al. 1989). As the amount of  $^{14}\text{C}$  in the equilibration solution is measured, any  $^{14}\text{C}$  labeled degradation product (i.e.  $\text{CO}_2$  or metabolites) in solution would lead to an underestimation of sorption (Wolf et al. 1989). An overestimation of sorption can occur if any metabolites or degradation products are sorbed or precipitated (Wolf et al. 1989).  $K_d$  is a sensitive input parameter in many pesticide fate and transport models, and can be used to predict the relative risk of pesticide movement to groundwater (Wagenet and Rao 1985, Brown et al. 1996, Coquet and Barriuso 2002).

The herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) is widely used for the post-emergent control of broadleaf weeds, particularly in cereal crops. Since 2,4-D has a small sorption potential in soil, it is a frequently detected herbicide in North American surface waters and groundwater (Goodrich et al. 1991, Rawn et al. 1999a). Soil organic matter is the single most important soil characteristic influencing 2,4-D retention by soil (Farenhorst et al. 2001).

As for most pesticides, soil organic carbon content also appears to be the single most important component controlling the retention of mercuric chloride by soil (Amacher et al. 1990). A competitive sorption between mercuric chloride and pesticides in soil would question the validity of using the soil sterilization technique in pesticide fate studies. The objective of this study was to quantify the effect of  $\text{HgCl}_2^-$  on the sorption of 2,4-D by soil, and how this effect may change depending on soil organic matter content and herbicide concentration.

### **3.3 Materials and Methods**

#### **3.3.1 Study site and soil sampling**

The study site was located in a gently undulating glacial till landscape (SE 32-14-25W) near Miniota, Manitoba. Soils in the study area belonged to the Newdale Association and were characterized by Black Chernozems based on the Canadian System of Soil Classification (Agriculture Canada Expert Committee on Soil Science 1987). The dominant texture of the surface soil (Ah) varied within the field from loam to clay loam.

A representative area (5.6 ha in size) was selected within the field, composed of ten parallel transects, each 11 m apart, and each 450 m long. For each transect, soil cores (3.7 cm diameter, 120 cm length) were collected by Manning (1999) with 21 sampling points in each transect, for a total of 210 sampling points. Sampling points were georeferenced using a Trimble 4600 LS global positioning system (Cansel, Winnipeg, Manitoba). Topographic characterization of the site was done on a 10 m grid, as described by Manning (1999) and in chapter 5.

Forty-five surface soil samples (Ah or Ahk) were chosen based on their soil organic carbon (SOC) content. The samples were selected such that there were a range of SOC levels for this study.

Using the site's elevation data and the MacMillan and Pettapiece (2000) Landform Description Program, the site was delineated into one of four different Landform Element Complexes (LECs): upper, middle, lower, and depressional slope positions. This LEC classification is based on differences in water distribution and soil development, which are calculated by the landform segmentation model (MacMillan and Pettapiece 2000). The program was run through Microsoft Visual FoxPro version 7 (Microsoft, Redmond, WA, 2001). The computed LECs were overlaid on the site's digital 3D elevation map using ArcView version 3.2 (ESRI, Redlands CA, 1999) in which the sampling points were assigned their appropriate LEC classification.

### **3.3.2 Soil property analysis**

Soil samples were air-dried and sieved (<2 mm) before analyses. Manning (1999) had analysed these samples for SOC and for pH. A LECO CHN 600 model was used to determine the %SOC content, which involved the dry combustion of 0.12g of oven-dried soil (Nelson and Sommers 1982). Inorganic carbon was removed before the organic carbon measurement by adding 6N HCl (Tiessen et al. 1983). Soil pH values were obtained using 20.0 mL of 0.01M CaCl<sub>2</sub> and 10g of air-dried soil (Hendershot and Lalonde 1993).

### 3.3.3 Herbicide sorption analysis

[U-ring-<sup>14</sup>C] 2,4-D (99% radiochemical purity; sp. act. 10 mCi mmol<sup>-1</sup>; American Radiolabeled Chemicals Inc. St. Louis, MO) and analytical-grade 2,4-D (95% purity, Sigma Chemical Co., St. Louis, MO) were used. The amount of radioactivity in the herbicide solutions was determined by liquid scintillation counting (LS 7500 Beckman Instruments, Fullerton, CA) using 5.0 mL of Scintisafe 30% scintillation cocktail (Fisher, Fairlawn, NJ).

The impact of soil sterilization by HgCl<sub>2</sub><sup>-</sup> on the extent of herbicide sorption by soil was determined using the batch-equilibrium procedure with and without HgCl<sub>2</sub><sup>-</sup> additions. Herbicide stock solutions were prepared by mixing the analytical-grade 2,4-D with [U-ring-<sup>14</sup>C] 2,4-D in 0.01 M CaCl<sub>2</sub> at a pH of 7.1. For the experiments with HgCl<sub>2</sub><sup>-</sup>, herbicide solutions were spiked at a rate of 0.5 g HgCl<sub>2</sub><sup>-</sup>/kg air-dry soil, which is comparable to other studies (Wolf et al. 1989, Fletcher and Kaufman 1980), and a factor of 10 times less than what was used in a recent study on the fate of benzene, toluene and xylene hydrocarbons in soil (Tsao et al. 1998).

Two sets of batch-equilibrium experiments were conducted. For the first set of experiments (n = 39 soil samples), the soil-water sorption partitioning coefficient was determined in triplicates using an initial herbicide concentration of 1 µg/mL of 2,4-D that contained 18 Bq of [U-ring-<sup>14</sup>C] 2,4-D. In the second set of experiments (n = 6 soil

samples), batch-equilibrium procedures were used to quantify the Freundlich distribution coefficient in duplicates. Initial herbicide concentrations used were 0.5, 1.0, 2.5, 5.0, and 10.0  $\mu\text{g/mL}$  of 2,4-D, and containing 0.9, 1.8, 4.5, 9.0, and 18.0 Bq of [U-ring- $^{14}\text{C}$ ] 2,4-D, respectively.

For each soil sample, 10.0 mL of the herbicide solution was added to 5.0 g of air-dry soil in 50 mL Teflon centrifuge tubes. The tubes were then placed in a rotary shaker for 24 hours at room temperature in the dark to reach equilibrium. Following equilibrium, the soil slurries were centrifuged at 10,000 rpm for 10 minutes and the supernatant was subsampled (1 mL) in duplicates to quantify the concentration of herbicides remaining in solution by liquid scintillation counting. Preliminary experiments revealed that no degradation of 2,4-D occurred over the 24 hour equilibrium period, both in the presence and absence of  $\text{HgCl}_2^-$ .

The amount of herbicide sorbed onto soil was determined by the difference between the initial and equilibrium herbicide concentrations. The Freundlich distribution coefficient,  $K_f$  [ $\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$ ], was quantified by nonlinear regression using the empirical Freundlich equation in the log transformation form:

$$\text{Log } C_s = \text{log } K_f + \frac{1}{n} \text{log } C_e \quad [1]$$

where  $C_s$  = the amount of 2,4-D sorbed per amount of soil [ $\mu\text{g/g}$ ],  $C_e$  = the 2,4-D concentration of the equilibrium solution [ $\mu\text{g/mL}$ ] and  $1/n$  = dimensionless Freundlich constant. The sorption distribution coefficient,  $K_d$  ( $\text{mL/g}$ ), was calculated assuming linear

partitioning ( $1/n = 1$ ):  $K_d = \left( \frac{C_s}{C_e} \right)$  [ 2]

where  $C_s$  is the concentration of 2,4-D in soil at equilibrium ( $\text{mg/g}$ ) and  $C_e$  is the concentration of 2,4-D in solution at equilibrium ( $\text{mg/mL}$ ). Greater  $K_d$  values denote more pesticide sorption by soil, relative to smaller  $K_d$  values.

All data and statistical analysis were performed using SigmaPlot 2000 (SPSS Inc. 2000a) and SigmaStat 2.03 (SPSS Inc. 2000b) and SAS version 8.01 (SAS Institute Inc. 2000). The Tukey's mean comparison test was used to compare the effects of the  $\text{HgCl}_2^-$  treatment on the herbicide sorption. Data were analysed for correlations using the Pearson pairwise correlation coefficient method. All statistical significance was set using  $P < 0.05$  as a significance level.

### 3.4 Results and Discussion

#### 3.4.1 The herbicide's soil-water partitioning coefficients ( $K_d$ )

Based on the MacMillan and Pettapiece (2000) landscape classification model there were 11, 15, 14, and 3 sampling points for the upper, middle, lower, and depressional LEC positions, respectively for this study.

The SOC content ranged from 1.17% to 3.85% with an average value of  $2.42\% \pm 0.56\%$  (standard deviation) ( $n=39$ ). Soil samples obtained from the depressional landscape positions showed significantly greater SOC content than samples from the lower, middle, and upper-slope positions (Table 3.1). Soil pH varied from 5.2 to 7.2 with an average value of  $6.4 \pm 0.5$  ( $n = 39$ ), but the pH spatial differences within the site were not influenced by their landscape position (Table 3.1).

The herbicide 2,4-D was weakly sorbed by soil.  $K_d$  values ranged from 0.1 mL/g to 0.8 mL/g and from 0.2 mL/g to 1.1 mL/g for batch equilibrium experiments with and without  $\text{HgCl}_2^-$ , respectively. Soil samples collected from different landscape positions varied in their sorption of 2,4-D by soil both in the presence and absence of  $\text{HgCl}_2^-$ , but differences were not statistically significant (Table 3.2). The mean  $K_d$  values increased from the upper to the middle LECs, then decreased in the lower LEC, and then increased again in the depressional LEC for both  $K_d$  with and without mercuric chloride. The  $K_d$  values obtained in this study resemble the values obtained by other studies for soils with

a similar organic matter content (Mallawatantri and Mulla 1992, Farenhorst et al. 2001). Herbicide sorption in the presence of  $\text{HgCl}_2^-$  was significantly correlated with both soil organic matter content and soil pH, except for the depressional slope positions, which had the smallest sampling size ( $n = 3$ ) (Table 3.3). For experiments without  $\text{HgCl}_2^-$ , herbicide sorption by soil was significantly correlated with SOC content, again except for samples from the depressional slope positions. Other studies have shown that soil organic matter is an important factor in the sorption of 2,4-D by soil and sediment (Farenhorst et al. 2001, Reddy and Gambrell 1987, Cheah et al. 1997).

Table 3.1 Mean values for %soil organic carbon and soil pH in relation to the landscape element complexes.

<b>LEC Position</b>	<b>% Soil organic carbon content</b>	<b>Soil pH</b>
All samples combined (n=39)	2.42 (0.56)	6.4 (0.5)
Samples from upper-slope positions (n=10)	2.18 <sup>1</sup> a <sup>2</sup> (0.68)	6.2 <sup>1</sup> a <sup>2</sup> (0.6)
Samples from middle-slope positions (n=13)	2.33 a (0.50)	6.3 a (0.4)
Samples from lower-slope positions (n=13)	2.51 a (0.39)	6.5 a (0.3)
Samples from depressional-slope positions (n=3)	3.19 b (0.45)	6.7 a (0.5)

<sup>1</sup> Means are followed by their standard deviation in brackets.

<sup>2</sup> Means followed by the same letter are not significantly different at  $P < 0.05$  (Tukey's mean comparison test).

Table 3.2 Sorption of 2,4-D by soil in relation to landscape position.  $K_d$  [mL/g] was determined by batch equilibrium experiments with and without mercuric chloride ( $HgCl_2^-$ ) additions.

LEC Position	$K_d$ with $HgCl_2^-$	$K_d$ without $HgCl_2^-$
All samples combined (n=39)	0.4 <sup>1</sup> a <sup>2</sup> (0.2)	0.6 <sup>1</sup> a <sup>2</sup> (0.2)
Samples from upper-slope positions (n=10)	0.4 a (0.2)	0.5 a (0.3)
Samples from middle-slope positions (n=13)	0.4 a (0.1)	0.6 a (0.2)
Samples from lower-slope positions (n=13)	0.4 a (0.1)	0.5 a (0.2)
Samples from depressional-slope positions (n=3)	0.5 a (0.2)	0.8 a (0.2)

<sup>1</sup> Means are followed by their standard deviation in brackets

<sup>2</sup> Means followed by the same letter are not significantly different at  $P < 0.05$  (Tukey's mean comparison test).

Table 3.3 Pearson correlation coefficients on the soil-water sorption partitioning coefficient ( $K_d$ ) with soil properties.  $K_d$  with and without mercuric chloride ( $HgCl_2^-$ ) additions. The significance levels are in brackets. (- = not significant at  $P < 0.05$ ).

a.  $K_d$  vs. %Soil organic carbon

	All Samples (n=39)	Upper (n=10)	Middle (n=13)	Lower (n=13)	Depressional (n=3)
$K_d$ with $HgCl_2^-$	0.61 (<0.01)	0.68 (0.03)	0.63 (0.02)	-	-
$K_d$ without $HgCl_2^-$	0.75 (<0.01)	0.80 (0.01)	0.61 (0.03)	0.83 (<0.01)	-

b.  $K_d$  vs soil surface pH

	All Samples (n=43)	Upper (n=11)	Middle (n=15)	Lower (n=14)	Depressional (n=3)
$K_d$ with $HgCl_2^-$	-0.43 (0.01)	-	-	-0.77 (<0.01)	-
$K_d$ without $HgCl_2^-$	-	-	-	-	-

The relation between SOC and herbicide sorption was stronger in the absence of the microbial inhibitor ( $r = 0.75$ ,  $P < 0.01$ , Figure 3.1a) than in the presence of  $\text{HgCl}_2^-$  ( $r = 0.60$ ,  $P < 0.01$ , Figure 3.1b). Also,  $K_d$  values obtained with the  $\text{HgCl}_2^-$  additions were smaller than those obtained without the microbial inhibitor (Table 3.2). These results suggest that  $\text{HgCl}_2^-$  competed with the 2,4-D molecules for sorption sites onto soil organic matter, thus decreasing the amount of 2,4-D sorbed by soil. The interference of  $\text{HgCl}_2^-$  with 2,4-D sorption increased with increasing SOC content (Figure 3.2). Organic matter is the single most important factor influencing the behaviour of Hg in the environment, including Hg retention by soil (Amacher et al. 1990).

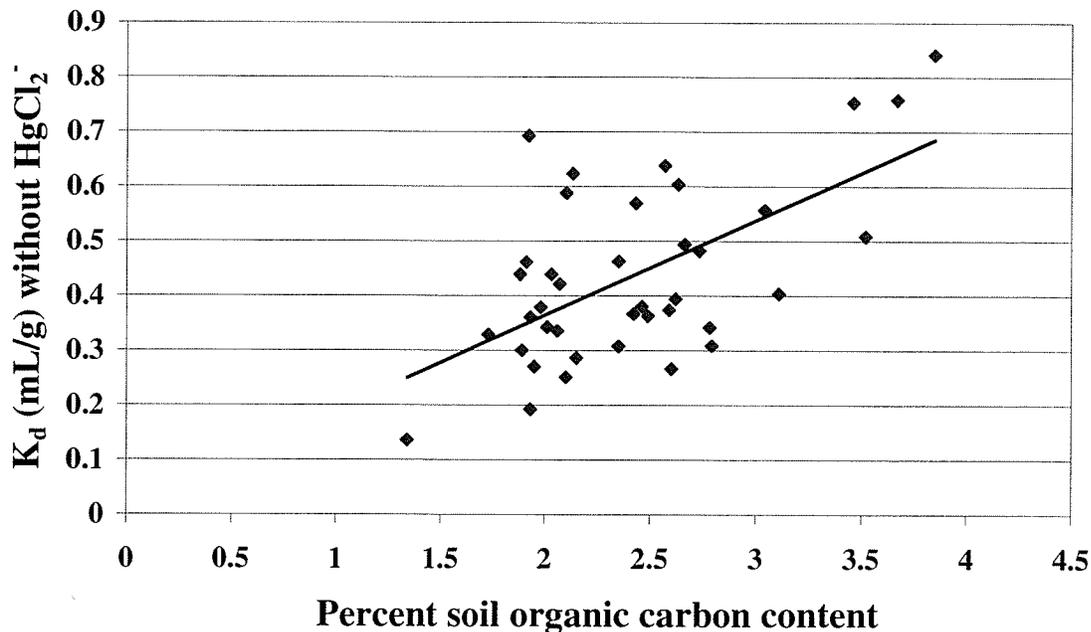


Figure 3.1a. Influence of SOC content on the soil-water partitioning coefficient ( $K_d$  in mL/g) for batch equilibrium experiments without  $\text{HgCl}_2^-$  ( $K_d = 0.31\% \text{SOC} - 0.17$ ,  $r = 0.75$ ,  $P < 0.01$ ).

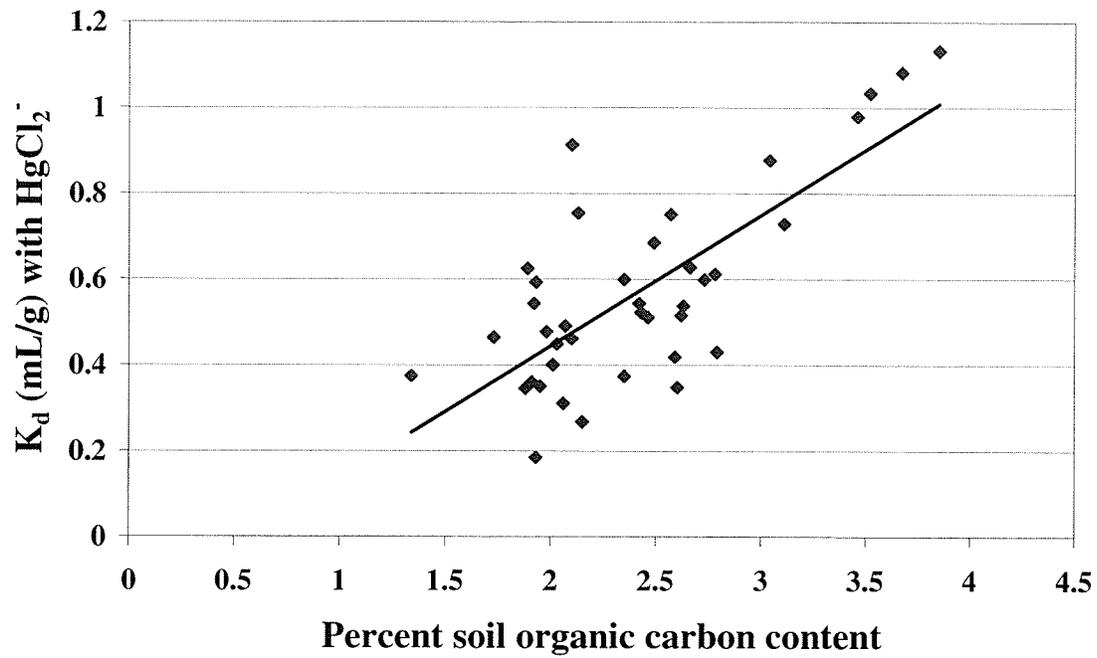


Figure 3.1b Influence of SOC content on the soil-water partitioning coefficient ( $K_d$  in mL/g) for batch equilibrium experiments with  $\text{HgCl}_2^-$  ( $K_d = 0.17\% \text{SOC} + 0.02$ ,  $r = 0.60$ ,  $P < 0.01$ )

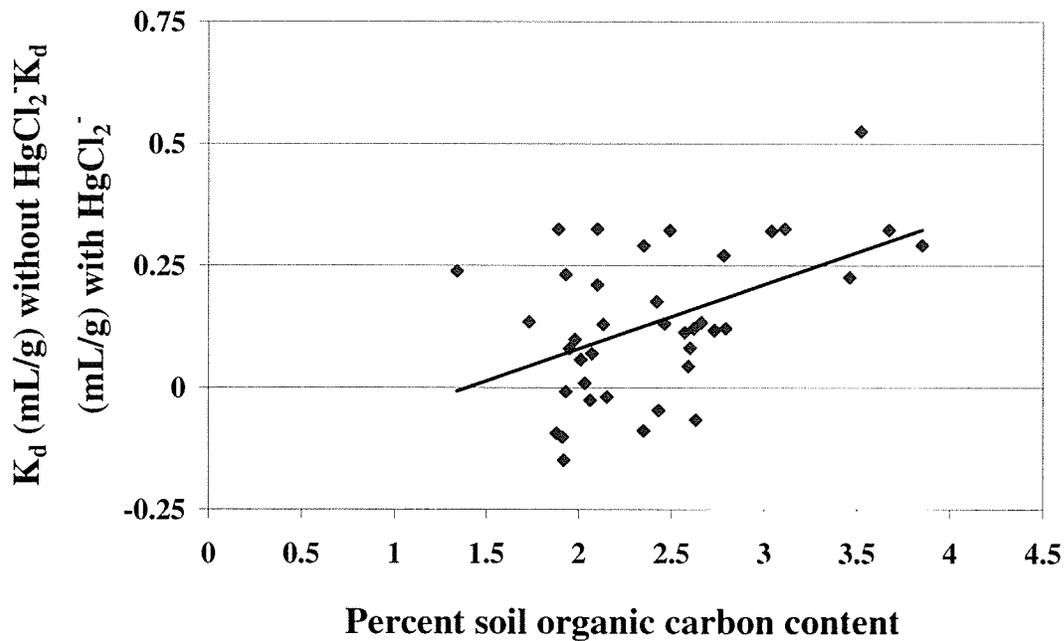


Figure 3.2 Influence of soil organic carbon content on the differences in soil-water sorption partitioning coefficient values ( $K_d$  in mL/g) between batch equilibrium experiments with and without  $\text{HgCl}_2^-$  ( $y = 0.13\% \text{SOC} - 0.18$ ,  $r = 0.48$ ,  $p < 0.01$ )

### 3.4.2 The herbicide's Freundlich distribution coefficient ( $K_f$ )

The Freundlich non-linear adsorption isotherms showed a very good fit to the measured data for all soil samples ( $r^2 > 0.97$ ,  $P < 0.01$ ). The Freundlich slope of the isotherms ( $1/n$ ) was less than unity with average values of  $0.73 \pm 0.03$  and  $0.72 \pm 0.02$ , for experiments with and without  $\text{HgCl}_2^-$ , respectively. This indicated that the affinity between the herbicide and the soil was greatest at initial low herbicide concentrations and decreased with increasing initial herbicide concentrations. As such, the Freundlich fitting

of 2,4-D isotherms was L-type (Giles et al. 1960), reflecting the saturation of the adsorption sites as the herbicide concentration increased.

The SOC content in the six samples ranged from 2.43% to 4.46% with an average of 3.44%. Herbicide sorption increased with increasing SOC content, both in the presence and absence of the microbial inhibitor (Table 3.5).  $K_f$  values ranged from 0.3 to 0.9  $\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$  and from 0.5 to 1.4  $\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$ , for batch equilibrium experiments with and without  $\text{HgCl}_2^-$ , respectively. Results of the Freundlich distribution coefficient experiments confirmed the  $K_d$  research findings described above in that  $K_f$  values from experiments without  $\text{HgCl}_2^-$  were consistently larger than the  $K_f$  values determined on the same soil in the presence of the  $\text{HgCl}_2^-$  (Table 3.4). Generally, the interference of  $\text{HgCl}_2^-$  with the herbicide sorption increased with increasing initial herbicide concentrations, but this relation was not always consistent amongst the five initial herbicide concentrations used.

Table 3.4 Freundlich distribution coefficient ( $K_f$  in  $\mu\text{g}^{1-1/n} \text{g}^{-1} \text{mL}^{1/n}$ ) as influenced by the absence or presence of a microbial inhibitor ( $\text{HgCl}_2^-$ ) in batch equilibrium experiments with soils at different soil organic carbon contents.

	Soil Organic Carbon Content [%]					
	2.43	2.83	3.31	3.55	4.02	4.46
$K_d$ with $\text{HgCl}_2^-$	0.3 <sup>1</sup> a <sup>2</sup> (0.02)	0.4 a (0.01)	0.5 a (0.05)	0.6 a (0.04)	0.9 a (0.02)	0.7 a (0.08)
$K_d$ without $\text{HgCl}_2^-$	0.5 b (0.06)	0.7 b (0.02)	0.6 a (0.02)	0.8 b (0.02)	1.1 b (0.03)	1.4 b (0.05)

<sup>1</sup> Mean of three replicates followed by standard deviation.

<sup>2</sup> Means followed by the same letter are not significantly different at  $P < 0.05$  (Tukey's mean comparison test).

This study demonstrated that soil sterilization techniques such as  $\text{HgCl}_2^-$  additions could influence the sorptive behaviour of pesticides in soil. These results support the findings of an earlier study (Fletcher and Kaufman 1980), which demonstrated that  $\text{HgCl}_2^-$  influenced the fate of the pesticide 3-chloroaniline in soil. Mercuric chloride has also been shown to be a reaction agent in the hydrolysis of organophosphorus pesticides (Wan et al. 1994). Adding mercuric chloride is not suitable as a soil sterilization technique in studies focusing on the fate of pesticides in soil. Additional studies are needed to define more appropriate soil sterilization techniques.

### 3.5 Summary and Conclusions

Using soil samples with different organic carbon contents (ranging from 1.34% to 4.46%) and different herbicide concentrations (ranging from 0.5 to 10 ug/mL), this study examined the influence of mercuric chloride additions to soil-water slurries on the sorptive behaviour of a phenoxy herbicide (2,4-D) in soil. Results indicated that mercuric chloride competed with the 2,4-D for sorption sites at all herbicide concentrations used. The interference of mercuric chloride with herbicide sorption increased with increasing SOC content. Mercuric chloride is a soil sterilization procedure that must not be used in herbicide fate studies as the retention of the mercuric chloride by soil strongly interfered with the capacity of the soil to retain the 2,4-D.

## **4. 2,4-D SORPTION AND DESORPTION IN SOIL IN RELATION TO SOIL VARIABILITY AND LANDSCAPE POSITION IN A CENTRAL WESTERN MINNESOTA HEAVILY TILLED AND ERODED LANDSCAPE**

### **4.1 Abstract**

The herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) is widely used for broadleaf weed control in cereal crops around the world. This study quantified the spatial variability of the sorption and desorption of 2,4-D in soil in a heavily tilled site near Morris, Minnesota. Herbicide sorption and desorption values for 301 soil samples were correlated to soil properties and to landscape position as classified by a landform description model. The herbicide was weakly bound to soil particles as evident by the low mean soil-water sorption partitioning coefficient ( $K_d$ ) value of 0.3 mL/g, the low mean organic carbon sorption partition coefficient ( $K_{oc}$ ) value of 24.5 mL/g, and because on average 48.7% of the sorbed herbicide readily desorbed back into soil solutions. Multiple linear regression between the  $K_d$  and soil properties revealed that %soil organic carbon (%SOC) was only able to weakly predict the herbicide's sorption behaviour. Instead, soil pH and carbonates had greater influences on the  $K_d$  values. Significant differences in the  $K_{oc}$  values throughout the landscape were found, therefore the amount of 2,4-D sorbed per unit of organic carbon varied with slope position. Significantly less herbicide desorption occurred in the upper slope positions compared to middle and lower

slope positions in which the herbicide desorption was predicted using pH,  $K_d$ , and  $K_{OC}$  as independent variables.

## 4.2 Introduction

Concerns have been raised about the potential for pesticides to leach into groundwater under areas of repeated annual pesticide applications (Miller et al. 1995a) and numerous occurrences of pesticide contamination into waterways have been reported throughout the United States (Mass et al. 1995) and in Canada (McRae 1989). One such pesticide that has been detected in both surface and groundwater samples is 2,4-Dichlorophenoxyacetic acid, (2,4-D) (Waite et al. 1992, Currie and Williamson 1995, Rawn et al. 1999a). This herbicide is widely used to control many broadleaf weeds in agricultural crops.

Designing better management practices that safeguard water quality, requires an understanding of the factors that affect the fate and movement of agricultural pesticides in soil (Mallawatantri et al. 1996). Two of these factors are pesticide sorption and desorption which influence the amount of pesticide residues that reach their target organisms, volatilize into the atmosphere, leach into groundwater, and are degraded (Cox et al. 1998). The intensity and extent of herbicide sorption and desorption are influenced by many soil properties (e.g. organic matter content and pH) and by the physical and chemical parameters of the sorbed compound (Oliveira Jr. et al. 1999, Sannino et al. 1997). Soil properties will vary spatially within landscapes because of the various soil formation processes. For example, soils at bottom slope positions tend to have greater soil organic matter content than soils in upper or middle slope positions (Mallawatantri

and Mulla 1992, Vink and Robert 1992, Khakural et al. 1994, Farenhorst et al. 2001). Soil properties within agricultural landscapes are also altered by tillage erosion, which usually causes soil loss on convex upper slope positions and soil accumulation on concave lower slope landscape positions. The tillage action also results in fewer amounts of crop residues being returned to the soil surface, accelerated organic matter decomposition, and increased losses of organic matter rich topsoil by wind and water erosion (Bowman et al. 1990, Arshad et al. 1990) relative to zero-tilled fields. With decreased amounts of soil organic matter in heavily-tilled sites, less pesticide sorption onto soil will occur.

Pesticide sorption onto soil is characterized by a partition constant  $K_d$ , with a subscript  $d$  (for distribution) (Wauchope et al. 2002). This  $K_d$  is a ratio of solid phases to solute concentration and is referred to the soil-water sorption partitioning coefficient (Wagenet and Rao 1985, Mallawatantri and Mulla 1992, Coquet and Barriuso 2002, Wauchope et al. 2002). High  $K_d$  values (of the order of 100 or greater) denote that the pesticide is strongly sorbed and is resistant to microbial degradation (Wauchope et al. 2002) and to leaching.

Since soil organic matter is usually the dominant factor in influencing the pesticide sorption by soil, the organic carbon sorption partition coefficient ( $K_{oc}$ ) is also used for quantifying pesticide sorption by soil (Rao and Davidson 1979, Coquet and Barriuso 2002, Wauchope et al. 2002).  $K_{oc}$  values are also frequently used as measures of

pesticide movement in soils and in fugacity models that describe the partitioning of pesticides in soil/water/atmosphere systems (Wauchope et al. 2002). The  $K_{OC}$  approach assumes that: (1) herbicides sorb only to soil organic carbon (SOC) (even at low organic carbon contents), (2) a linear relation exists between  $K_d$  and SOC (even at low organic carbon contents), and (3) SOC has a continuous sorption capacity (Mallawatantri and Mulla 1992, Green and Karickhoff 1990). Opinions differ about the legitimacy of the  $K_{OC}$  method for environmental applications from support (Chiou et al. 1979) to skepticism (Mingelgrin and Gerstl 1983).

The objective of this study was to quantify the spatial variability of soil properties and 2,4-D sorption and desorption by soil in a heavily-tilled eroded field.

## **4.3 Materials and Methods**

### **4.3.1 Study site description**

The study site is situated in Nora Township, Pope County (SW-1/4-31-126N-40W) near Morris, Minnesota. This site has been cultivated for approximately 100 years in which it has been annually moldboard plowed for the past 40 years (Lindstrom et al. 2000). This has redistributed the soil within the site in that soil erosion was identified by the exposure of calcareous material at the surface in the upper shoulder landscape positions (Lindstrom et al. 2000). A wheat and soybean crop rotation has been grown on the site for the past

five years. Several different herbicides, including 2,4-D, were applied to the field during this time (Table 4.1).

Table 4.1 The herbicides and active ingredients that have been applied to the Morris site (M. Lindstrom person. comm. 2002).

<b>Herbicides applied</b>	
<b>Product Name</b>	<b>Active Ingredient</b>
Prowl	Pendimethalin
Treflan	Trifluralin
Pursuit	Imazethapyr
2,4-D	2,4-D
Banvel	Dicamba

Diedrick (1972) surveyed and classified the soils at the site as mostly being of the Mollisol soil order based on the United States soil taxonomy, which corresponds to the Canadian classification of Chernozemic soils. The soil series on the site are: Barnes, Buse, Darnen, Estelline, Langhei, Parnell, and Svea. The Svea is the most predominate series on the site. Most of these soils are fine loamy, deep, and are moderately to well drained (T. Schumacher 2002 person. comm.). The Barnes, Buse and the Langhei series are mostly located on convex landscape positions while the Darnen, Svea, and Parnell series are frequently situated on concave landscape positions (T. Schumacher 2002 person. comm.). A more detailed description of these soil series is given in Appendix IA.

### 4.3.2 Experimental design

Placed over the site's 4 ha were 16 adjacent transects spaced at 10 m intervals. Each transect was 180 m long and had 18 sampling points (Figure 4.1). An additional 16 sample points were placed throughout an ephemeral gully, which was on the western side of the field site. In total, 304 samples were taken. However, only 301 of these samples were analysed for this study because three samples were lost.

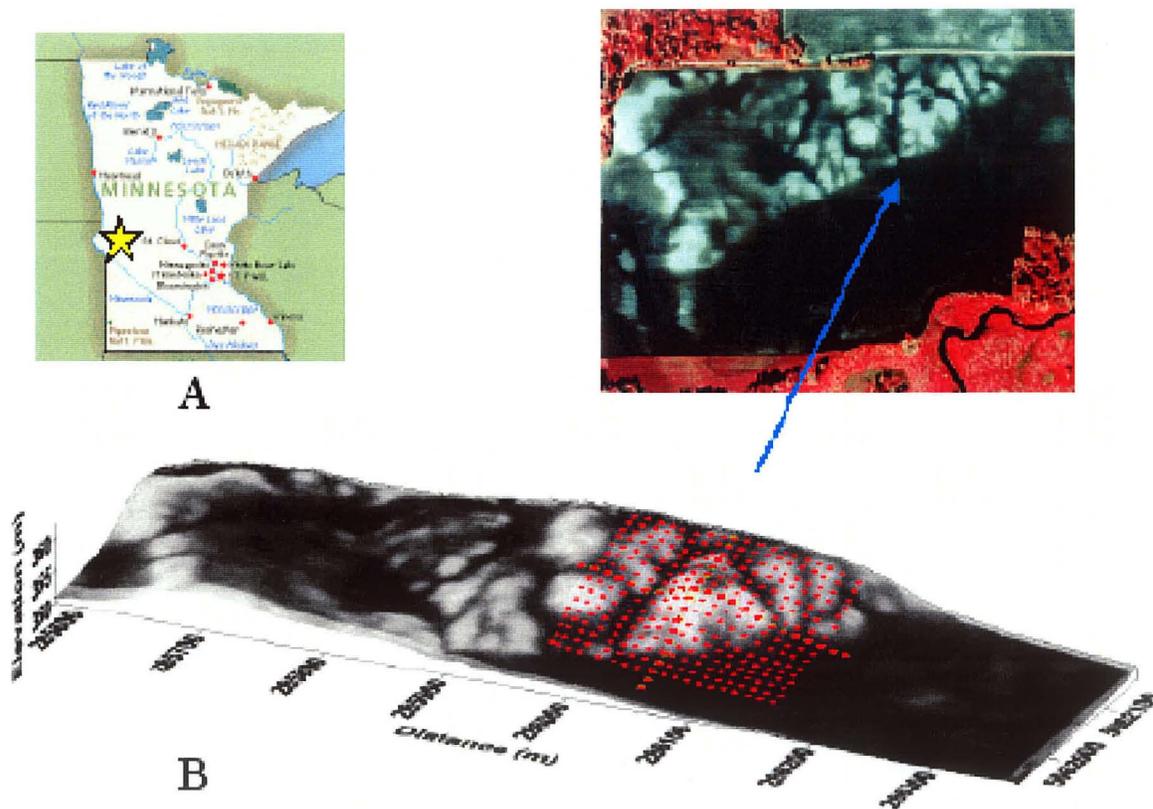


Figure 4.1(a) Map of Minnesota indicating study site location and (b) a 3D aerial photograph of the Morris site showing the eroded shoulders and the location of the sampling points (adapted from T. Schumacher 2002 person. comm.).

The elevations of the 304 sampling points were determined by interpolation from the original survey grade elevation data set that was measured with a Leica Survey Grade DGPS system on a 10 m by 10 m grid (M. Lindstrom 2001 person. comm.). The points were collected and marked with a Trimble AG132 DGPS unit using a Radcal differential corrections service (J. Schumacher 2002 person. comm.).

The soil samples were collected in late August of 2000 with the use of a 3 inch Giddings hydraulic probe (M. Lindstrom 2001 person. comm.). The samples were taken by 15 cm increments to a depth of 45 cm (M. Lindstrom 2001 person. comm.). Only soil samples from the 0-15 cm depth were used for this study, in which the samples were first thoroughly mixed, air-dried, and ground (<2 mm).

#### **4.3.3 Soil sample analyses**

All soil samples were analysed for % soil organic carbon content (%SOC), pH, percent total carbonates (percent calcite + percent dolomite), and for 2,4-D sorption and desorption. A LECO 2000 CNS model was used to determine the %SOC content, which involved the dry combustion of 0.2 g of oven-dried soil (Nelson and Sommers 1982). Before the %SOC measurement, the inorganic carbon was removed by adding 10 mL of 6N HCl to every sample (Tiessen et al. 1983). Subsequently, the samples were rinsed clean of leftover chlorine with deionized water and suction filtered, then oven dried at 110 °C. Soil pH values were determined by weighing 10.0 g of soil into 50 mL centrifuge tubes with 20.0 mL of 0.01M CaCl<sub>2</sub>. The samples were then shaken for 30 minutes and pH was recorded with a glass electrode when the reading stabilized

(Hendershot and Lalonde 1993). Total carbonates (percent calcite + percent dolomite) were analysed on a percentage basis by a method adapted from Loeppert and Suarez (1996). This carbonate determination method involved adding a HCl-FeCl<sub>2</sub> solution to soil samples and measuring the amounts of evolved CO<sub>2</sub> after 30 seconds of shaking (for the calcite measurement) and then after 30 minutes of shaking (for the dolomite measurement). Soil particle size analysis was determined by the pipette method (Loveland and Whalley 1991) on 48 samples that were randomly chosen from the 301 samples

#### **4.3.4 Batch equilibrium experiments**

##### **4.3.4.1 2,4-D sorption onto soil**

The amount of 2,4-D sorption by soil was determined in duplicates for each soil sample. The herbicide stock solutions were made by first adding 1.0 mg/L of analytical-grade 2,4-D (95% purity, Sigma Chemical Co., St. Louis, MO.) into a 0.01 M CaCl<sub>2</sub> solution at a pH of 7.1. Approximately 19 Bq/L of [U-ring-<sup>14</sup>C] 2,4-D (99% radiochemical purity; sp. act. 10 mCi/mmol; American Radiolabeled Chemicals Inc. St. Louis, MO.) was then mixed into the stock solution. Herbicide solution (10.0 mL) was added to 5.0 g of air-dried soil into 50 mL Teflon centrifuge tubes. The tubes were then placed in a rotary shaker for 24 hours at room temperature in the dark to reach equilibrium. Following a 24 hour equilibrium period, the soil slurries were vortexed, centrifuged at 10,000 rpm for 10 minutes, and the supernatant was subsampled in 1.0 mL duplicates.

Previous batch experiments have shown that 2,4-D sorption on soil occurs rapidly, with most of the herbicide being removed from solution within the first few hours, and that a 24 hour equilibrium period is sufficient to characterize the second phase of slow sorption (Sannino et al. 1997, Wauchope et al. 2002). Preliminary testing revealed that 2,4-D did not adsorb onto the Teflon centrifuge tubes.

A Liquid Scintillation Counter (LSC) (LS 7500 Beckman Instruments, Fullerton, CA) was used to measure the amount of [U-ring-<sup>14</sup>C] 2,4-D in equilibrium solutions, with 5.0 mL of ScintiSafe 30% scintillation cocktail (Fisher, Fairlawn NJ.) added to each subsampled (1.0 mL) supernatant. The amount of herbicide sorbed on soil was determined by the difference between the initial and equilibrium herbicide concentrations.

The sorption distribution coefficient,  $K_d$  (mL/g), was calculated assuming linear

partitioning ( $1/n = 1$ ): 
$$K_d = \left( \frac{C_s}{C_e} \right) \quad [1]$$

where  $C_s$  is the concentration of 2,4-D in soil at equilibrium (mg/g) and  $C_e$  is the concentration of 2,4-D in solution at equilibrium (mg/mL). Greater  $K_d$  values denote more pesticide sorption by soil, relative to smaller  $K_d$  values.

The organic carbon sorption partition coefficient ( $K_{oc}$ ) was calculated by normalizing the 2,4-D  $K_d$  values for soil organic carbon by using the following equation (Novak et al.

$$1997): \quad K_{oc} = \left( \frac{K_d}{\%SOC} \right) \times 100 \quad [2]$$

#### 4.3.4.2 Percent 2,4-D desorption by soil

After the aliquots were sampled for 2,4-D sorption, the remaining supernatant was removed and replaced by a 0.01 M  $CaCl_2$  solution at a pH of 7.1. The samples were then rotated again for 24 hours in the dark at room temperature to allow equilibrium to reach. After being vortexed and centrifuged at 10,000 rpm for 10 minutes, the supernatant of each sample was subsampled (1.0 mL) in duplicates to quantify the remaining [U-ring- $^{14}C$ ] 2,4-D in solution by the LSC.

Percent herbicide desorption was calculated on a total [U-ring- $^{14}C$ ] 2,4-D basis:

$$\left( \frac{A}{B} \right) \times 100\% \quad [3]$$

where A is the total amount of [U-ring- $^{14}C$ ] 2,4-D in soil solution following desorption and B is the total amount of [U-ring- $^{14}C$ ] 2,4-D in soil following sorption.

#### 4.3.5 Statistical methods

Using the site's elevation data and the MacMillan and Pettapiece (2000) Landform Description Program, the site was delineated into one of three different Landform

Element Complexes (LECs): upper, middle, and lower slope positions. This LEC classification is based on differences in water distribution and soil development, which are calculated by a landform segmentation model (MacMillan and Pettapiece 2000). The program was run through Microsoft Visual FoxPro version 7 (Microsoft, Redmond, WA. 2001). The computed LECs were overlaid on the site's digital 3D elevation map using ArcView version 3.2 (ESRI, Redlands CA. 1999) in which the 301 sampling points were assigned their appropriate LEC classification.

Surfer<sup>TM</sup> gridding and contouring software version 6.0.4 (Golden Software, Boulder CO. 1997) with the Kriging method was utilized to produce the 3D data maps. JMP IN version 3.1.5 statistical software program (SAS Institute Inc. 1995) was used to produce the side-by-side quantile boxplots to graphically display the data distributions within each LEC.

Parametric statistical analyses are not valid unless the data follows certain necessities such as having normality and equal variances. In eroded fields, the distributions of soil properties are often skewed, thus preventing the use of parametric statistics, unless the variables are transformed (Rogowski et al. 1990). Therefore, all collected data were analysed for normality using the Shapiro-Wilk W test and for equal variances using the Levene's test. All non-normal data were first transformed to attain a normal distribution (Table 4.2). Data that did not conform to normality despite the various transformation attempts were analysed using the non-parametric multiple median comparison method of the Kruskal-Wallis test as described by Daniel (1990). For the normal data, the Tukey's

multiple mean comparison tests were used. All data were then analysed for correlations using the Pearson pairwise correlation coefficient method. Stepwise regression analyses using all of the data were also performed. During the regression analyses, all of the independent variables were also checked to determine if they were related by use of the variance inflation factor test. All statistical tests were done using the SAS statistical software program version 8.01 (SAS Institute Inc. 2000). All statistical significance was set using  $P < 0.05$  as a significance level.

Table 4.2 Assessing if the variables are normalized with or without transformation

Variable	None	Transformation Type			
		$\text{Log}_{10}(x+1)$	$\sqrt{x}$	$x^2$	$\frac{1}{x}$
A horizon Depth	No	No	No	No	No
%Total Carbonates	No	No	No	No	No
Surface pH	No	No	No	No	No
%SOC	No	Yes	N/A	N/A	N/A
$K_d$	No	No	No	No	No
$K_{oc}$	No	No	No	No	No
%Herbicide Desorption	No	No	No	Yes	N/A
%Clay	No	No	No	No	No

Legend: No = Data set did not follow a normal distribution  
 Yes = Data set followed a normal distribution and thus was analysed using the Tukey's mean comparison test  
 N/A = transformation was not needed, because data had been normalized

## 4.4 Results and Discussion

### 4.4.1 Soil properties and herbicide behaviour across the landscape

#### 4.4.1.1 The variability of the soil properties and herbicide behaviour

Only 193 of the 304 samples were analysed for the site's A horizon depth because this property was not recorded for each sampling point when the samples were collected. The A horizon depth varied across the landscape from 17 cm to 32 cm with an average value of 25 cm  $\pm$  4 cm (standard deviation), and had a median value of 25 cm (Figure 4.2a). The percent total carbonates (percent calcite + percent dolomite) varied from 0.0% to 25.9%, had a mean of 5.3%  $\pm$  5.8%, and had a median of 2.4% (Figure 4.2b). The %total carbonate's distribution was heavily skewed with many samples having little or no carbonates. However, in 61 samples large quantities of carbonates (i.e. >10.0%) were determined indicating that the original surface horizon was eroded and was mixed with the carbonate-rich subsoil horizon in some locations within the site.

The soil surface pH varied from 6.85 to a maximum of 7.85 in which its mean was 7.56  $\pm$  0.19 (Figure 4.2c), and its median was 7.48. Percent clay was determined on 48 samples only, which had a mean of 15.6%  $\pm$  4.5%, a median of 15.9%, in which the average texture was a loam soil. The site's average sand content was 47.1%  $\pm$  8.7% and the average silt content was 37.3%  $\pm$  9.6%.

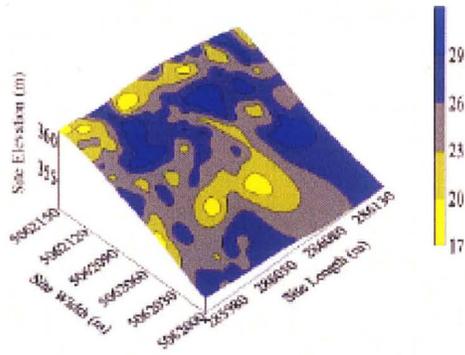


Figure 4.2a The spatial distribution of the Ap horizon depth (cm.)

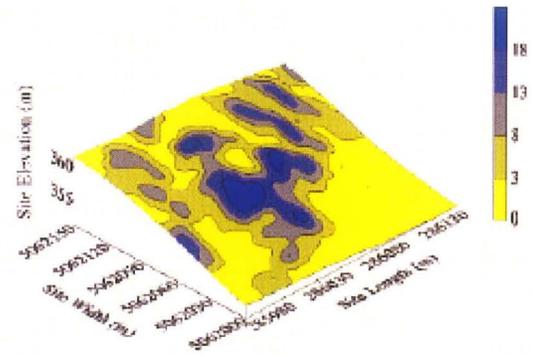


Figure 4.2b The spatial distribution of percent total carbonates

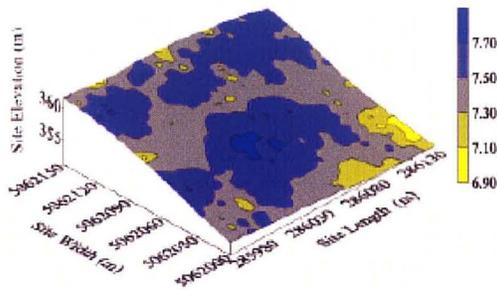


Figure 4.2c The spatial distribution of soil surface pH

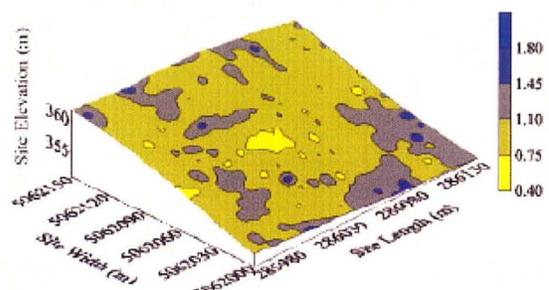


Figure 4.2d The spatial distribution of percent soil organic carbon content

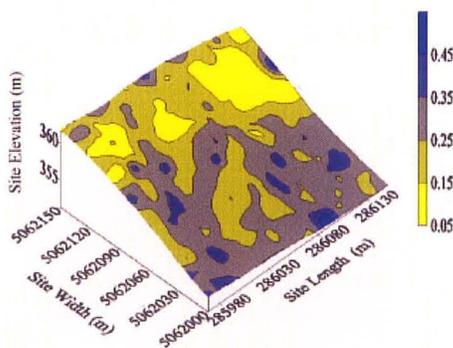


Figure 4.2e The spatial distribution of the herbicide's  $K_d$  (mL/g)

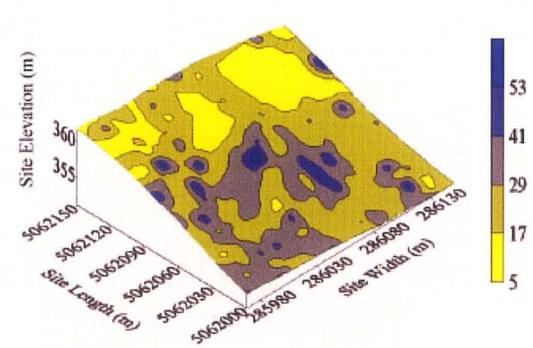


Figure 4.2f The spatial distribution of the herbicide's  $K_{oc}$  (mL/g)

Percent soil organic carbon content (%SOC) was overall low since it varied from 0.38% to a maximum of 1.97%, with an average of  $1.03\% \pm 0.28\%$ , and its median was 0.98% (Figure 4.2d). In an untilled grassland field adjacent to this site, which had the same soil series as the tilled site, ten surface samples were taken the same time the tilled site soil samples were taken. When these samples were analysed for %SOC, the average was  $3.16\% \pm 0.70\%$ . This indicates that the tilled site's SOC content had been drastically reduced compared to this nearby grassland field. This observed reduction in soil organic carbon content in the surface horizons at the tilled site is partly because the surface soil has been redistributed and mixed with the subsurface soil due to the tillage (Lindstrom et al. 2000). Usually soil organic carbon concentrations in the plow layer decrease quickly for several years after cultivation and then stabilize (Paustian et al. 1997). Tillage decreases soil organic carbon contents by disturbing aggregates and exposing previously inaccessible soil organic matter to microbial decomposition (Dexter 1988). As well, soil organic carbon in some areas within the landscape may be lost as tillage increases the soil's susceptibility to wind and water erosion (Kachanoski et al. 1992, Lobb et al. 1995).

The herbicide's soil-water partitioning coefficient,  $K_d$ , had an average of  $0.3 \text{ mL/g} \pm 0.1 \text{ mL/g}$ , a median of  $0.2 \text{ mL/g}$ , and ranged from  $0.1 \text{ mL/g}$  to  $0.6 \text{ mL/g}$  (Figure 4.2e). This average  $K_d$  value is lower than those 2,4-D  $K_d$  values obtained by Mallawatantri and Mulla (1992) and by Farenhorst et al. (2001). However in these two studies, greater amounts of SOC existed which contributed significantly to those greater  $K_d$  values.

Johnson et al. (1995) studied 2,4-D sorption onto two Arkansas soils, which had organic matter that ranged from 0.5% to 1.0% and obtained 2,4-D  $K_d$  values of 0.59 mL/g and 0.50 mL/g (for two pH 5 soils), and  $K_d$  values of 0.19 mL/g and 0.12 mL/g (for two pH 7 soils). As such, the results for the Morris site were similar to the results of the neutral pH soils by Johnson et al. (1995).

The herbicide's organic carbon sorption partition coefficient,  $K_{OC}$ , had an overall mean of 24.5 mL/g  $\pm$  11.5 mL/g, and a median of 23.4 mL/g. The  $K_{OC}$  values extended from 5.5 mL/g to 57.2 mL/g throughout the landscape (Figure 4.2f). This low mean  $K_{OC}$  value again indicates that the sorption of the herbicide to the soil particles was quite weak. In addition, this mean  $K_{OC}$  value is much lower than the mean 2,4-D  $K_{OC}$  values obtained by Rao and Davidson (1979) who obtained 2,4-D  $K_{OC}$  values of 119.4 mL/g for a silty clay loam Iowa soil, 72.2 mL/g for a sandy loam soil from Georgia, and 135.7 mL/g for a fine sand soil from Florida. Cheah et al. (1997) determined that the average 2,4-D  $K_{OC}$  values were 43.9 mL/g  $\pm$  53.1 mL/g and 17.3 mL/g  $\pm$  4.2 mL/g for a Malaysian sandy loam and a muck soil, respectively.

On average, 48.7%  $\pm$  11.1% of the sorbed herbicide desorbed back into the soil solutions (Figure 4.2g). The percentage of sorbed herbicide that desorbed ranged from 7.9% to 74.3%, and had a median of 51.1%. This again indicates that the herbicide was generally weakly bound to the soil constituents and will be mobile in the soil matrix. Cheah et al.

(1997) determined that just over 20% of sorbed 2,4-D desorbed back into soil solutions using two Malaysian soils.

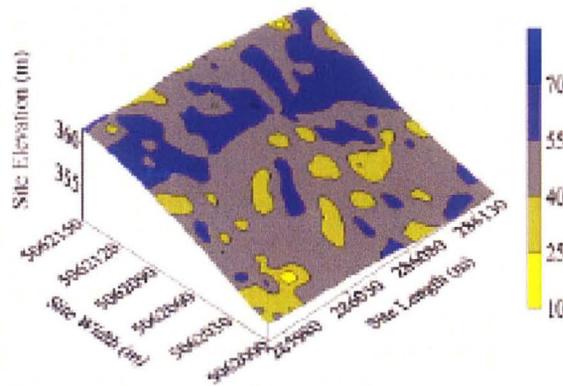


Figure 4.2g The spatial distribution of % 2,4-D desorption.

#### 4.4.1.2 Correlations between soil properties and the herbicide behaviour

Total carbonates had a weak negative correlation with %SOC (Table 4.3,  $r = -0.35$   $P < 0.01$ ). The correlation between %SOC and total carbonates is due to the tillage erosion, which caused for increased amounts of calcareous, organically-poor subsoil material to be brought to the surface, and for the SOC content to decrease.

Across 193 points, surface pH was only weakly correlated to A horizon depth ( $r = -0.15$ ,  $P = 0.03$ , Table 4.3). Over all sampling points, the soil surface pH was adequately correlated with %total carbonates ( $r = 0.55$ ,  $P < 0.01$ ) (Table 4.3). These correlations were not surprising since carbonates with an alkaline character act as pH buffers in the soil. Overall, the surface soils were moderately alkaline most likely because of the tillage erosion. The calcareous subsoil material that was exposed on abrupt convex slope positions had been redistributed over the landscape because of the tillage erosion

Table 4.3 Pearson correlation coefficients between all soil properties for all sampling points. (- = not significant at  $P < 0.05$ , \* = significant at  $P < 0.05$ , \*\* = significant at  $P < 0.01$ )

	%SOC	Surface pH	Percent total carbonates	Ah depth	$K_d$	$K_{oc}$	Percent herbicide desorption	% Clay
%SOC	1.00							
Surface pH	-0.37**	1.00						
Percent total carbonates	-0.35**	0.55**	1.00					
Ah depth (n=193)	-	-0.15**	-	1.00				
$K_d$	0.23**	-0.42**	-0.36**	-	1.00			
$K_{oc}$	-0.42**	-0.12*	-	-	0.75**	1.00		
%Herbicide desorption	-	0.14*	-	-	-0.60**	-0.50**	1.00	
%Clay (n=48)	-	-	-	-	-	-	-	1.00

(Lindstrom et al. 2000) on the severely eroded knolls. This then increased the surface soil pH (Lindstrom et al. 2000). In a tilled site in South Dakota, Gollany et al. (1992) also noticed that the soil pH increased as the amount of free CaCO<sub>3</sub> at the surface increased.

The herbicide's K<sub>d</sub> was not significantly correlated with %clay content. The 2,4-D's K<sub>d</sub> was only weakly related to %SOC ( $r = 0.23$ ,  $P < 0.01$ , Figure 4.3), which is opposite to what other researchers found who have all determined that %SOC was strongly correlated to 2,4-D sorption by soil (Grover 1973, Reddy and Gambrell 1987, Mallawatantri and Mulla 1992, Johnson et al. 1995, Cheah et al. 1997, Farenhorst et al. 2001). These researchers examined fields that were much less eroded than the Morris site. Therefore, the results of this study suggest that soil erosion dramatically affects the behaviour of the 2,4-D in soils by removing soil organic matter as a factor in models predicting 2,4-D sorption by soil.

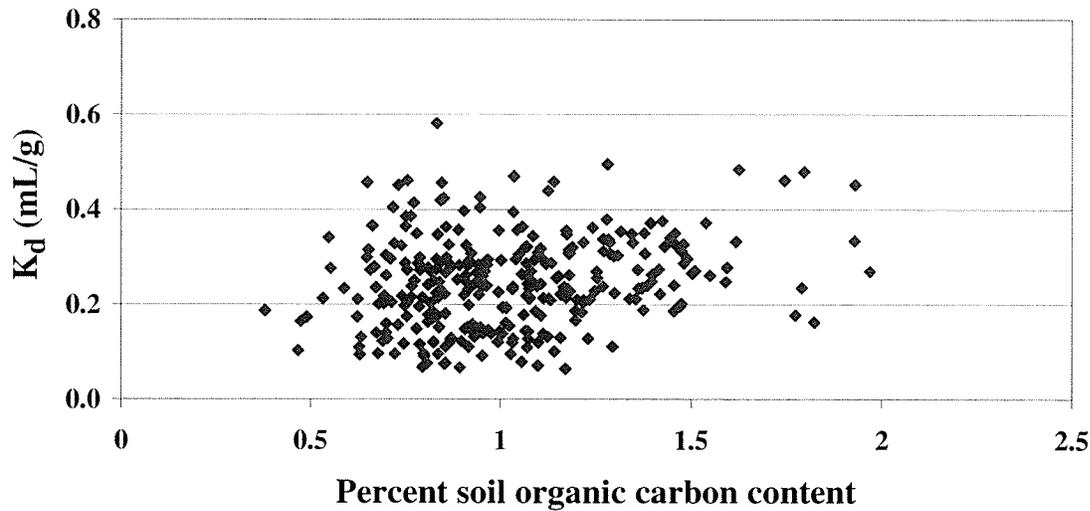


Figure 4.3 Relation between %SOC and the adsorption partition coefficient ( $K_d$ ) for 2,4-D ( $K_d = 0.17 + 0.08\%SOC$ ,  $r = 0.23$ )

The tillage erosion decreased the %SOC content and increased the quantities of carbonates present in the surface soils. Over all points, the herbicide's  $K_d$  was weakly negatively correlated to percent total carbonates ( $r = -0.36$ ,  $P < 0.01$ ). Although, 2,4-D sorption directly onto the carbonates was not measured, these correlations do indicate that in soils with more carbonates present, the soil constituents sorbed less herbicide.

With less %SOC content present and an increased soil pH, herbicide sorption onto the soil particles was decreased. Increased 2,4-D sorption was moderately negatively correlated to soil pH (Figure 4.4). As the pH of the soil samples increased, the herbicide molecules in the solutions were losing more protons, thus becoming more anionic, and thus had less affinity for negatively charged soil surfaces (Hermosin and Cornejo 1991). As such, this study found that the herbicide sorption occurred preferentially at a low soil

pH, when 2,4-D was in molecular form, whereas the anionic form of the herbicide, that was favoured at high soil pH, had less affinity for the soil surfaces.

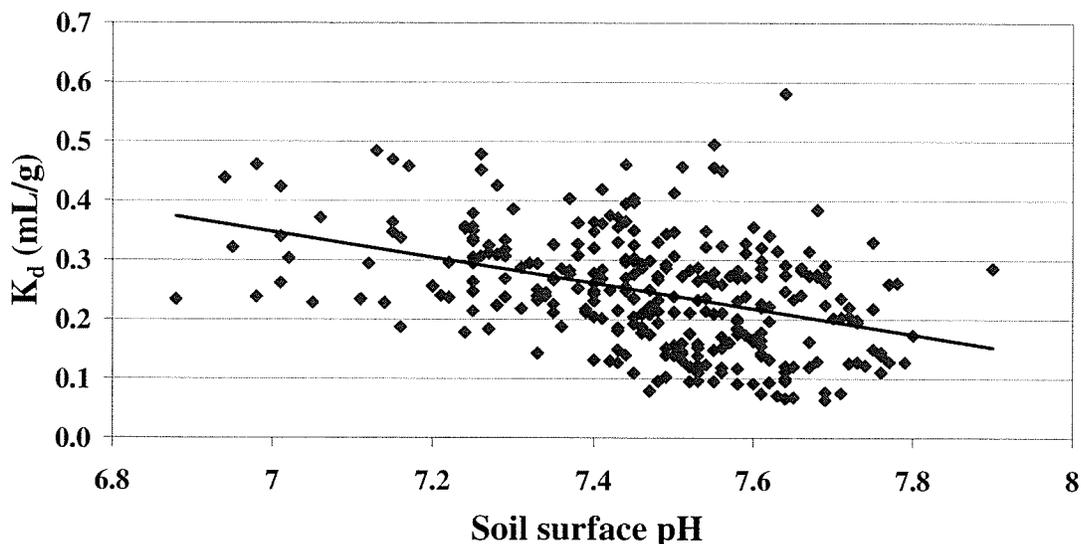


Figure 4.4 Relation between the adsorption partition coefficient ( $K_d$ ) and soil surface pH. ( $K_d = 1.89 - 0.22pH$ ,  $r = -0.42$ ,  $P < 0.01$ )

The lower pH of the soil could have resulted in more of the herbicide and the soil's functional groups being in the molecular form (Johnson et al. 1995). This may have caused increased herbicide sorption from one or more of the following: (a) hydrogen bonding through the herbicide's acid group onto the negatively charged cation exchange capacity; (b) protonation of the acid group on the herbicide by protons from the functional groups and (c) partitioning of the herbicide molecules into the organic phase of the soil (Johnson et al. 1995). Johnson et al. (1995) also determined that 2,4-D sorption onto soil was affected by soil pH in that the 2,4-D  $K_d$  values were greater at pH 5 than at pH 7.

The herbicide's  $K_{OC}$  was moderately negatively correlated to %SOC (Figure 4.5). This indicated that soils with greater SOC contents sorbed less 2,4-D per unit of organic carbon, relative to soils with lesser organic carbon contents. This further suggested that the soil organic matter quality may have influenced 2,4-D sorption by soil and that other soil properties may have influenced the extent of 2,4-D sorption onto the soil organic carbon. For example, soil pH decreased with increasing SOC content, thus enhancing the portion of 2,4-D in molecular form (versus the anionic form) and thus the amount of 2,4-D sorbed. The herbicide's  $K_{OC}$  was strongly correlated with  $K_d$  ( $r = 0.75$ ,  $P < 0.01$ ). However, the spatial distributions of  $K_{OC}$  and  $K_d$  were not the same, which also appear to suggest that other soil properties were involved in the 2,4-D sorption besides SOC.

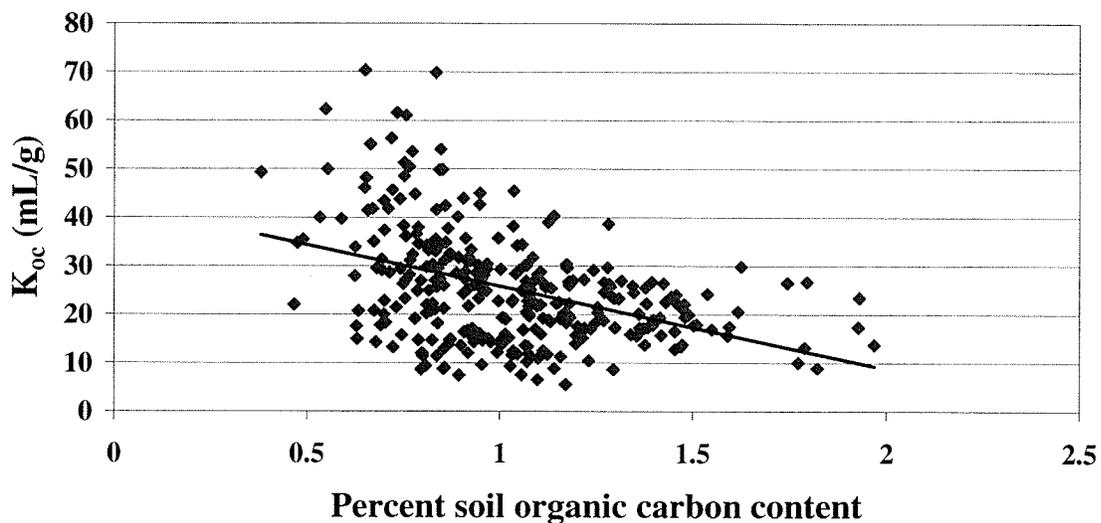


Figure 4.5 Relation between percent soil organic carbon content and the organic carbon partition coefficient ( $K_{OC}$ ) for 2,4-D ( $K_{OC} = 42.83 - 17.07\%SOC$ ,  $r = -0.42$ )

Percent 2,4-D desorption was weakly correlated with pH ( $r = -0.14$ ,  $P = 0.01$ ) and was moderately correlated with both  $K_d$  ( $r = -0.60$ ,  $P < 0.01$ ) and  $K_{OC}$  ( $r = -0.50$ ,  $P < 0.01$ )

(Table 4.3). Since the herbicide desorption was negatively correlated with  $K_d$ , this indicated that as more of the herbicide was sorbed by soil, less 2,4-D readily desorbed back into the soil solutions. The amount of sorbed herbicide that desorbed was not significantly correlated with %SOC (Figure 4.6), or with clay content. This indicates that a given soil property alone could not explain the strength of 2,4-D sorption by soil, excluding soil properties (e.g. iron oxides) that were not measured in this study.

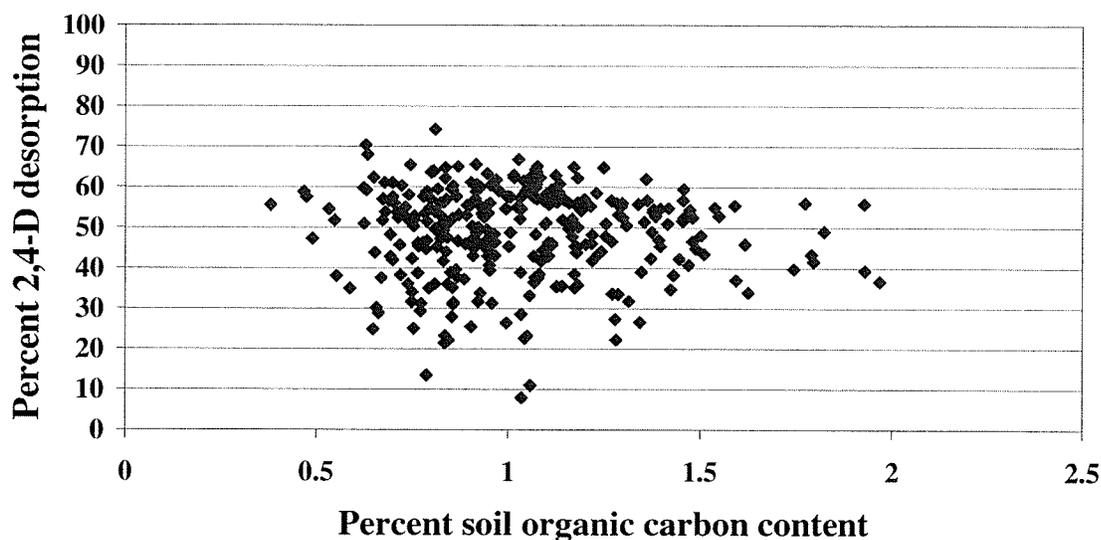


Figure 4.6 Relation between %soil organic carbon and % 2,4-D desorption  
 (% Desorption =  $50.46 - 1.68\%SOC$ ,  $r = -0.04$ )

#### 4.4.1.3 Predicting herbicide behaviour with the soil properties

Soil properties and stepwise linear regression were used to predict the herbicide's sorption and desorption behaviour. Percent SOC alone was only able to weakly predict  $K_d$  with  $r = 0.23$  ( $K_d = 0.17 + 0.1\%SOC$ ,  $P < 0.01$ , Figure 4.3). This is opposite to what other researchers have found who determined that %SOC was able to predict 2,4-D's  $K_d$

(Mallawatantri and Mulla 1992, Farenhorst et al. 2001). This might be explained by three possible theories: (1) little variability existed in the range of the SOC (0.38% to 1.97%) which may have contributed to the poor  $K_d$  prediction ability of the SOC; and (2) the sorption of the 2,4-D by soil was very weak making  $K_d$  predictions difficult for the Morris site. Also, the herbicide sorption did not strongly increase with increasing amounts of %SOC, therefore other soil properties or factors may have been involved in the sorption of the herbicide.

Soil surface pH alone was able to best predict  $K_d$  with  $r = -0.42$  ( $K_d = 1.85 - 0.21\text{pH}$ ,  $P < 0.01$ , Figure 4.4). The pH status of the soil media can influence the ionic status of the herbicide, which determines the type and amount of bonding that occurred (Grover 1973, Weber et al. 1993). Percent total carbonates gave  $r = -0.36$  in its  $K_d$  prediction model ( $K_d = 0.28 - 0.01\%\text{Total carbonates}$ ,  $P < 0.01$ ). The herbicide would have predominately been in its anionic form during the sorption experiments. Some research has shown that carbonates may sorb anions. Jurinak and Griffin (1972) reported that pure calcite adsorbed  $\text{NO}_3^-$ . However, soil  $\text{CaCO}_3$  did not adsorb the  $\text{NO}_3^-$  as competing anions in the soil solution or coatings on the carbonate mineral surfaces interfered with the  $\text{NO}_3^-$  adsorption (Jurinak and Griffin 1972). In this Morris study, the 2,4-D was negatively charged during the sorption experiments and the 2,4-D may have been sorbed onto the soil  $\text{CaCO}_3$  with or without any interference by other anions. Predicting  $K_d$  with all of the soil properties combined produced a non-significant model.

Other soil properties, which were not measured in this study, could have attributed to the sorption of the 2,4-D onto soil. One such property is the soil's cation exchange capacity. For example, Reddy and Gambrell (1987) reported that the cation exchange capacity for 19 soils and sediments helped to explain the extent of 2,4-D sorption behaviour. Iron oxides have also been shown to sorb 2,4-D. Focusing on ferrihydrite, goethite, and lepidocrocite, Clausen and Fabricius (2001) found that  $K_d$  values for these iron oxides decreased with increasing pH due to electrostatic interactions between the oxide surface and the 2,4-D anionic form. Watson et al. (1973) determined that 2,4-D's sorption behaviour onto goethite was also pH dependent in that maximum sorption occurred near the  $pK_a$  of the herbicide and decreased with increasing pH. As such, in this Morris study, the sorption of 2,4-D onto iron oxides may have occurred but would most likely be small since the pH of the soil samples was well above the 2,4-D  $pK_a$  values of 2.64 - 2.87.

Clausen et al. (2001) found that 2,4-D was able to sorb to synthetic calcite and quartz when the mineral surfaces contained positively charged sites. The pesticide was weakly attached to the minerals through electrostatic forces through the compounds'  $COO^-$  groups (Clausen et al. 2001). However, quartz and calcite only played a minor role in the 2,4-D sorption process as compared to clay and possible oxide minerals (Clausen et al. 2001).

Percent clay content did not have an effect on the herbicide sorption. The soil clay particles had a net negative charge and therefore had little affinity for the negatively

charged 2,4-D molecules. This low adsorptive capacity of clays for 2,4-D, including negative adsorption (i.e. repulsion), has been reported by Weber et al. (1965), Grover (1971), and by Cheah et al. (1997).

Percent herbicide desorption was adequately predicted by the herbicide's  $K_d$  ( $\% \text{ Desorption} = 65.92 - 69.8K_d$ ,  $r = -0.60$ ,  $P < 0.01$ ). Soil pH gave a very poor prediction of percent herbicide desorption with  $r = 0.14$  ( $\% \text{ Desorption} = -15.08 + 8.54\text{pH}$ ,  $P = 0.01$ ). Predicting herbicide desorption with the other soil properties, alone or combined, produced non-significant models.

#### **4.4.2 Soil properties and herbicide sorption and desorption by soil in relation to landform element complexes**

The MacMillan and Pettapiece (2000) Landform Description Program delineated the 304 sampling points into one of three different Landform Element Complexes (LECs): upper, middle, and lower slope positions (Figure 4.7). A total of 100, 138, and 63 sampling points were allocated to upper, middle, and lower LECs, which encompassed 33%, 46%, and 21% of the 301 points, respectively. Unlike the Miniota site (chapters 3 and 5), none of the Morris' sampling points were located in a depressional LEC.

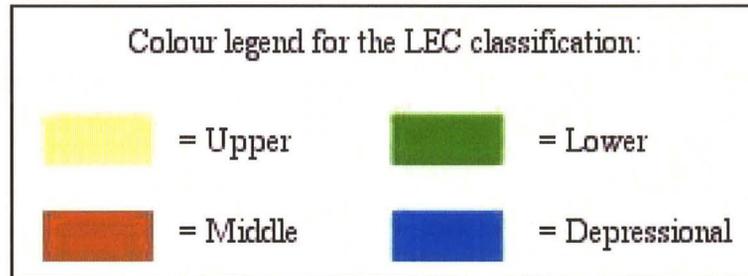
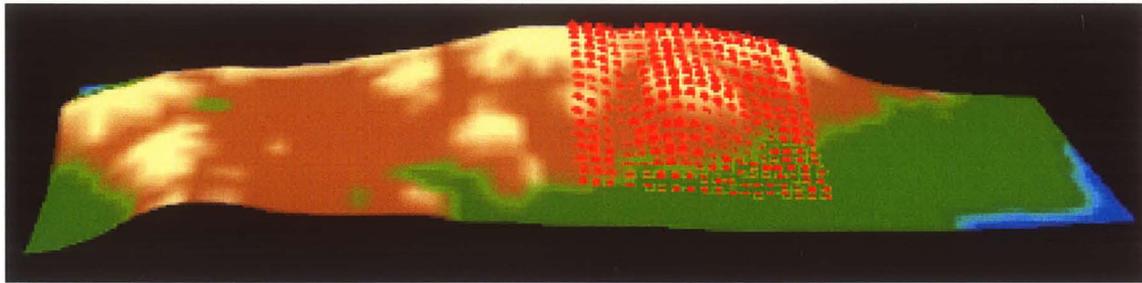


Figure 4.7 The site's LEC delineations by the MacMillan and Pettapiece (2000) landform description program and the locations of the sampling points.

#### 4.4.2.1 The variability of the soil properties and herbicide behaviour

The average A horizon depth values slightly increased from the upper LEC (25 cm  $\pm$  4 cm) to the middle LEC (25 cm  $\pm$  4 cm) and again increased to the lower LEC (26 cm  $\pm$  3 cm). The median A horizon depths was 25 cm for both the upper and middle LECs and was 27 cm in the lower LEC, in which no significant differences among the LECs occurred (Figure 4.8a).

The percent total carbonates' mean amounts were 7.5%  $\pm$  8.1%, 5.6%  $\pm$  6.7%, and 0.9%  $\pm$  1.6% for the upper, middle, and lower LECs, respectively. The median values decreased from the upper LEC (4.5%) to the middle LEC (2.5%) to the lower LEC (0.4%) (Figure 4.8b). The lower LEC had significantly less total carbonates, relative to

the other LECs, because of topsoil erosion from the middle and upper LECs and subsequent deposition in the lower LEC.

Usually, when HCl is added to samples of the soil series that are present in the site, no effervescence (due to a reaction of the HCl and the carbonates) is observed until reaching the B<sub>k</sub> or C<sub>k</sub> horizons, except for the Langhei series, which normally exhibits a slight effervescence throughout the soil profile (Lindstrom et al. 2000). However, several of the surface soil samples located on convex slope positions exhibited severe effervescence when the HCl was applied to soil from the Ap horizons, which indicated that the transport and mixing of free CaCO<sub>3</sub> into the tilled layer had occurred (Lindstrom et al. 2000).

Brubaker et al. (1993) who focused on Nebraska silt loam and silty clay soils reported that CaCO<sub>3</sub> amounts generally increased downslope. This was attributed to the CaCO<sub>3</sub> containing soil series, which were present in the lower slope positions and that less net soil erosion and greater leaching had occurred on lower slopes than on upper slope positions. In a tilled South Dakota site, Gollany et al. (1992) noticed that where topsoil had been removed in the Ap horizon due to soil erosion, there was an increase in the free CaCO<sub>3</sub> on the surface, which is what occurred at Morris.

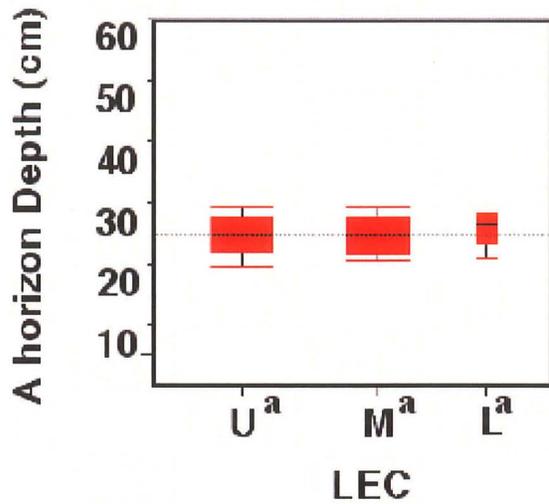


Figure 4.8a A horizon depth distribution by LEC<sup>1</sup>

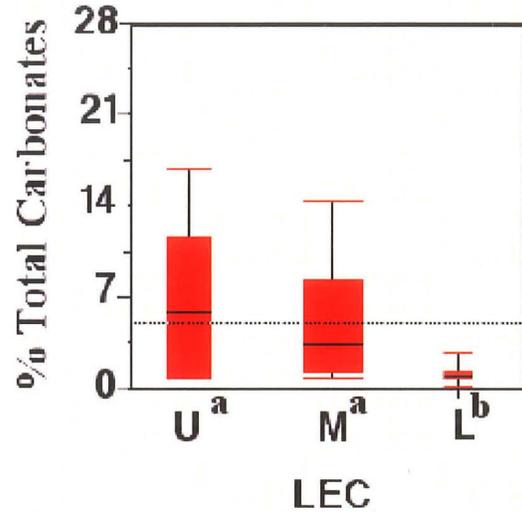


Figure 4.8b Percent total carbonates distribution by LEC<sup>1</sup>

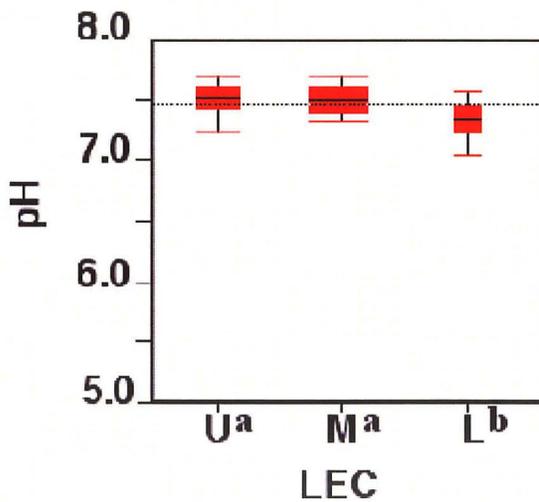


Figure 4.8c Soil surface pH distribution by LEC<sup>1</sup>

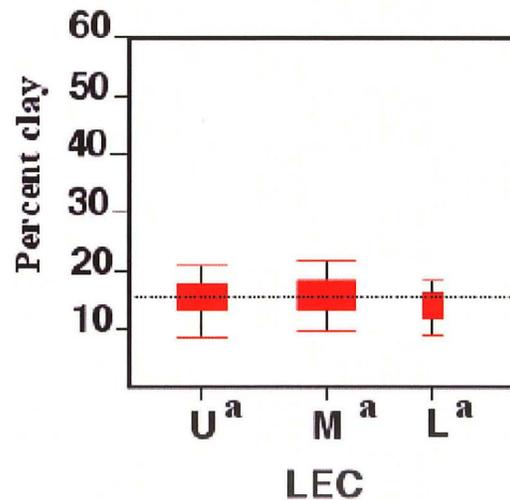


Figure 4.8d Percent clay content distribution by LEC<sup>1</sup>

1. These quantile boxes graphically display the distribution of the each variable across the LECs. The groups' medians are shown as a line across the middle of each figure and the quartiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) are as its ends (SAS Institute Inc. 1995). The 10<sup>th</sup> and 90<sup>th</sup> quantiles are shown as lines above and below the box (SAS Institute Inc. 1995). Same letters beside the LECs indicates that the medians or means of the distributions are not significantly different at  $P < 0.05$ . The larger the sample size, the wider are the quantile boxes.

The average pH values across the LECs were  $7.55 \pm 0.20$ ,  $7.54 \pm 0.14$ , and  $7.41 \pm 0.19$  for the upper, middle, and lower LECs, respectively. The median soil surface pH values decreased slightly from the upper LEC (7.53) to the middle LEC (7.51) and then decreased significantly to the lower LEC (7.32) (Figure 4.8c). Mallawatantri and Mulla (1992) found that soil pH decreased significantly from upper to bottom slope positions in a Washington State site. Similar to Mallawatantri and Mulla's (1992) study, the more alkaline pH in the upper slope positions of the Morris site was most likely due to the exposure of subsoil material that was more basic than the surface soil.

The average %clay values for the LECs were  $16.1\% \pm 3.7\%$ ,  $15.7\% \pm 4.8\%$ , and  $14.2\% \pm 5.6\%$  for the upper, middle, and lower LECs, respectively. The amount of clay in the soil samples did not significantly differ among the LECs since the median values were 15.9% (upper), 15.8% (middle), and 16.4% (lower) (Figure 4.8d).

The site's %SOC average distribution across the LECs decreased from the upper LEC ( $1.01\% \pm 0.24\%$ ) to the middle LEC ( $0.97\% \pm 0.27\%$ ), and then increased to the lower LEC ( $1.16\% \pm 0.32\%$ ) (Figure 4.8e). The median amounts of %SOC across the LECs were 1.03% (upper), 0.92% (middle), and 1.13% (lower), whereby the amount of %SOC in the lower LEC was significantly greater than in the other LECs. Again, this variability in %SOC may have been caused by differences in the landscape's erosional, carbon and nitrogen mineralization, and depositional processes.

The mean  $K_d$  values across the LECs were  $0.2 \text{ mL/g} \pm 0.0 \text{ mL/g}$ ,  $0.3 \text{ mL/g} \pm 0.0 \text{ mL/g}$ , and  $0.3 \text{ mL/g} \pm 0.0 \text{ mL/g}$  for the upper, middle, and lower LECs, respectively. The herbicide's median  $K_d$  values increased significantly from the upper LEC ( $0.2 \text{ mL/g}$ ) to the middle LEC ( $0.3 \text{ mL/g}$ ) to the lower LEC ( $0.3 \text{ mL/g}$ ) (Figure 4.8f).  $K_d$  increased with decreasing slope position because of greater %SOC and lower soil pH conditions at the lower slopes, relative to the upper and middle LECs. Mallawatantri and Mulla (1992) had a similar spatial distribution of 2,4-D  $K_d$  values within a Washington State site. Novak et al. (1997) also determined that atrazine  $K_d$  values were lower on shoulder positions compared to depressional positions in an Iowa site. This Iowa site also had increasing amounts of SOC from upper to lower landscape positions, which appeared to have accounted for the increased atrazine sorption by soils in these lower slope positions (Novak et al. 1997).

The average  $K_{oc}$  values were  $20.7 \text{ mL/g} \pm 11.0 \text{ mL/g}$ ,  $27.2 \text{ mL/g} \pm 11.4 \text{ mL/g}$ , and  $28.8 \text{ mL/g} \pm 10.5 \text{ mL/g}$  for the upper, middle, and lower LECs, respectively. The 2,4-D's  $K_{oc}$  median values increased significantly from the upper LEC ( $18.2 \text{ mL/g}$ ) to the middle LEC ( $25.9 \text{ mL/g}$ ) to the lower LEC ( $26.6 \text{ mL/g}$ ) (Figure 4.8g). This demonstrates that the sorptive capacity of the soil organic matter was not the same across the site. Specifically, the sorptive capacity of the organic carbon decreased with increasing %SOC contents ( $r = -0.42$ , Figure 4.5) and decreasing landscape positions. The upper LEC had

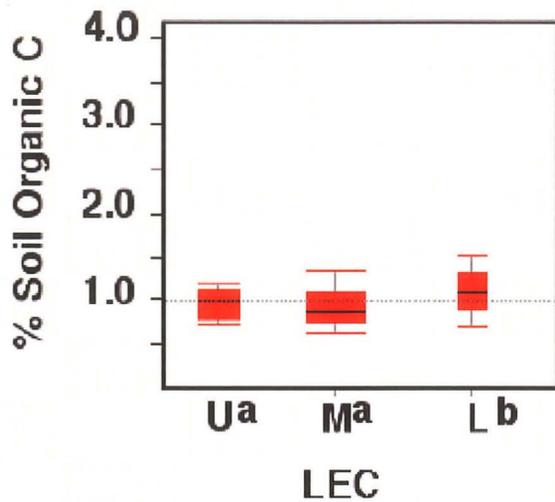


Figure 4.8e % Soil organic carbon distribution by LEC<sup>1</sup>

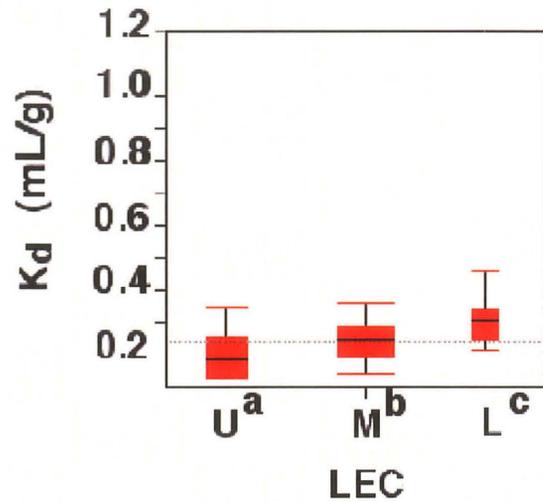


Figure 4.8f The herbicide's  $K_d$  distribution by LEC<sup>1</sup>

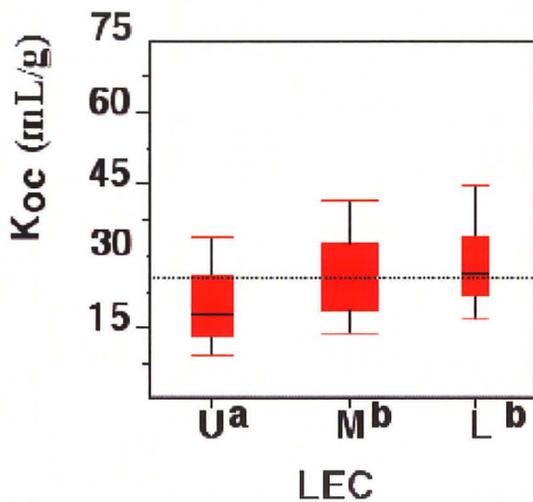


Figure 4.8g The herbicide's  $K_{oc}$  distribution by LEC<sup>1</sup>

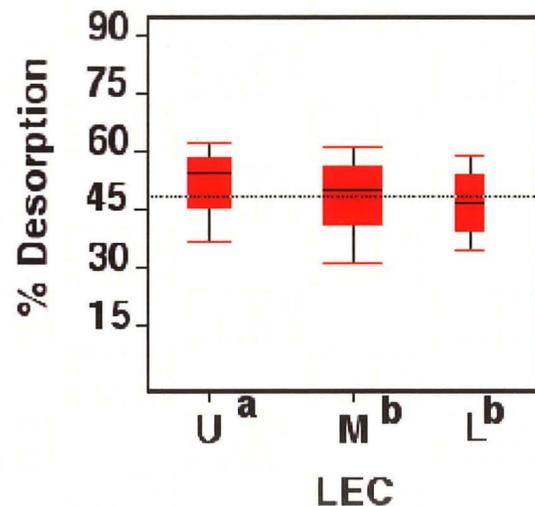


Figure 4.8h % Herbicide desorption distribution by LEC<sup>1</sup>

1. These quantile boxes graphically display the distribution of the each variable across the LECs. The groups' medians are shown as a line across the middle of each figure and the quartiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) are as its ends (SAS Institute Inc. 1995). The 10<sup>th</sup> and 90<sup>th</sup> quantiles are shown as lines above and below the box (SAS Institute Inc. 1995). The same letters beside the LECs indicates that the medians (or means for percent desorption) of the distributions are not significantly different at  $P < 0.05$ . The larger the sample size, the wider are the quantile boxes.

a significantly smaller average  $K_{OC}$  value perhaps due to the greater soil carbonate content that may have been interfering with the 2,4-D sorption onto the soil organic carbon. Alternatively, this result could also suggest that the organic matter quality influenced the extent of the 2,4-D sorption. This would imply that SOC was not the only factor in the sorption of the 2,4-D. In contrast, Mallawatantri and Mulla (1992) determined that the sorptive capacity of SOC in a Washington State site increased with increasing organic carbon content as evident by the lack of a single  $K_{OC}$  value for 2,4-D and three other pesticides.

The mean amounts that the herbicide desorbed decreased from the upper LEC ( $51.6\% \pm 10.6\%$ ) to the middle LEC ( $47.8\% \pm 10.9\%$ ) to the lower LEC ( $46.4\% \pm 11.3\%$ ) (Figure 4.8h). The upper LEC significantly desorbed more 2,4-D, relative to the middle and lower LECs. This suggests that 2,4-D was less strongly sorbed in upper slope positions, and may have been from variability in the herbicide's  $K_d$  distribution since  $K_d$  and percent herbicide desorption were moderately correlated across all points. As well in the upper LEC, the herbicide was more in its anionic state, due to the greater soil pH, which could indicate that the anionic form is released from the soil more easily, relative to the other LECs.

#### 4.4.2.2 Correlations between the soil properties and herbicide behaviour

Percent total carbonates were correlated with %SOC in the upper, middle, and lower LECs ( $r = -0.40$ ,  $P < 0.01$ , Table 4.4,  $r = -0.30$ ,  $P < 0.01$ , Table 4.5, and  $r = -0.27$ ,  $P = 0.03$ , Table 4.6, respectively). These correlations between the carbonates and %SOC occurred because the tillage action exposed the carbonate-rich organically poor subsoil material at the surface, particularly in the upper and middle LECs, and decreased the amount of SOC. Additional analyses by Tsai (2003, unpublished data) confirmed that the Morris subsoil material contained less SOC than the original topsoil.

Soil pH was also correlated to percent total carbonates in the lower LEC, ( $r = 0.43$ ,  $P < 0.01$ ), middle LEC,  $r = 0.57$ , ( $P < 0.01$ ), and in the upper LEC,  $r = 0.50$ , ( $P < 0.01$ ). The soil's pH was weakly correlated to %SOC across all LECs with  $r = -0.32$  ( $P < 0.01$ ),  $r = -0.30$  ( $P < 0.01$ ), and  $r = -0.41$  ( $P < 0.01$ ) in the upper, middle, and lower LECs, respectively. The surface pH was also weakly correlated with the depth of the A horizon in the upper and middle LECs with values of  $r = -0.32$  ( $P = 0.04$ ) and  $r = -0.49$  ( $P < 0.01$ , Tables 4.4 and 4.5, respectively).

$K_d$  was not significantly correlated with %SOC in any of the LECs. This was unexpected as soil organic carbon has been reported as the predominant sorbent of most pesticides as long as the total organic carbon is larger than 0.1% (Schwarzenbach and Westall 1981), including 2,4-D (Grover 1973, Reddy and Gambrell 1987, Mallawatantri and Mulla 1992, Johnson et al. 1995, Cheah et al. 1997, Farenhorst et al. 2001). However, if %SOC is below 0.1%, interactions with mineral surfaces may be more important (Pignatello

Table 4.4 Pearson pairwise correlation coefficients between all soil properties for the upper LEC sampling points only (n = 100).  
 (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	Percent total carbonates	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00							
Surface pH	-0.32**	1.00						
Percent total carbonates	-0.40**	0.50**	1.00					
Ah depth (n=94)	-	-0.21*	-	1.00				
K <sub>d</sub>	-	-0.50**	-	-	1.00			
K <sub>oc</sub>	-0.24*	-0.27*	-	-	0.85**	1.00		
%Herbicide desorption	-	-	-	-	-0.66**	-0.47**	1.00	
%Clay (n=19)	-	-	-	-	-	-	-	1.00

Table 4.5 Pearson pairwise correlation coefficients between all soil properties for the middle LEC sampling points only (n = 138).  
 (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	Percent total carbonates	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00							
Surface pH	-0.30**	1.00						
Percent total carbonates	-0.30**	0.57**	1.00					
Ah depth (n=88)	0.30**	-0.49**	-0.27*	1.00				
K <sub>d</sub>	-	-0.24**	-0.34**	-	1.00			
K <sub>oc</sub>	-0.50**	-	-	-	0.76**	1.00		
%Herbicide desorption	-	-	-	-	-0.56**	-0.50**	1.00	
%Clay (n=21)	-	-	-	-	-	-	-	1.00

Table 4.6 Pearson pairwise correlation coefficients between all soil properties for the lower LEC sampling points only (n = 63).  
 (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	Percent total carbonates	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide Desorption	%Clay
%SOC	1.00							
Surface pH	-0.41**	1.00						
Percent total carbonates	-0.27*	0.43**	1.00					
Ah depth (n=10)	-	-	-	1.00				
K <sub>d</sub>	-	-	-	-	1.00			
K <sub>oc</sub>	-0.68**	-	-	-	0.50**	1.00		
%Herbicide desorption	-	-	-	-	-0.55**	-0.44**	1.00	
%Clay (n=8)	-	-	-	N/A	-	-	-	1.00

1989). The organic carbon content in the Morris soil samples ranged from 0.38% to 1.97% such that the mineral surfaces could only play a moderate role in the sorption of the 2,4-D by soil. Also, the herbicide's  $K_d$  was not correlated to percent clay content in any of the LECs (Tables 4.4, 4.5, and 4.6). Therefore, other soil properties besides %SOC and clay minerals determined the 2,4-D's sorption behaviour in soil for this strongly eroded landscape.

$K_d$  was significantly correlated with carbonates and pH in the upper and middle LECs (Tables 4.4 and 4.5). In the upper LEC,  $K_d$  was moderately correlated to pH ( $r = -0.50$ ,  $P < 0.01$ ). In the middle LEC,  $K_d$  was weakly correlated with %total carbonates ( $r = -0.34$ ,  $P < 0.01$ ), and soil pH ( $r = -0.24$ ,  $P = 0.01$ ). Johnson et al. (1995) and Hermosin and Cornejo (1991) also observed a decreased 2,4-D sorption onto soil with increased soil pH.

The herbicide's  $K_{oc}$  correlation with %SOC varied within the LECs with  $r = -0.29$  ( $P < 0.01$ ) in the upper LEC to  $r = -0.50$  ( $P < 0.01$ ) in the middle LEC to  $r = -0.68$  ( $P < 0.01$ ) in the lower LEC. Since the strength of the correlations between  $K_{oc}$  and SOC varied, this indicates that the sorption capacity of the soil organic carbon varied with landscape position. The sorption of the 2,4-D per unit of organic carbon was more strongly responsive to increasing amounts of soil organic carbon in soil samples of the lower LEC relative to the other LECs. This may be due to the less alkaline pH soil in the lower LEC

relative to the middle and upper LECs. With a more alkaline pH in the upper and middle LECs compared to the lower LEC, more of the 2,4-D was in its anionic form and less was sorbed compared to the 2,4-D molecular form. As well, more carbonates were present in the upper and middle LECs compared to the lower LEC, and as such may have interfered with the sorption of the herbicide onto the soil organic matter.

For each LEC, the coefficient of correlations values between  $K_{oc}$  and  $K_d$  varied from 0.85 ( $P < 0.01$ ) to 0.76 ( $P < 0.01$ ), to 0.50 ( $P < 0.01$ ) for the upper, middle, and lower LECs, respectively (Tables 4.3, 4.4, 4.5).  $K_{oc}$  in each LEC had a similar strength of relation with percent herbicide desorption with  $r = -0.47$  ( $P < 0.01$ ) in the upper LEC to  $r = -0.50$  ( $P < 0.01$ ) in the middle LEC to  $r = -0.44$  ( $P < 0.01$ ) in the lower LEC. Since the strength of the correlations between  $K_{oc}$  and  $K_d$  varied within the LECs, soil properties other than SOC, may have affected the 2,4-D sorption and desorption onto the soil constituents.  $K_{oc}$  was not significantly correlated with % clay content in any of the LECs.

In the upper LEC, % herbicide desorption was correlated with  $K_d$  ( $r = -0.66$ ,  $P < 0.01$ ), %SOC ( $r = -0.24$ ,  $P = 0.02$ ), and with pH ( $r = 0.33$ ,  $P < 0.01$ , Table 4.4). In the middle and lower LECs, % herbicide desorption was correlated with  $K_d$  ( $r = -0.56$ ,  $P < 0.01$ , Table 4.5,  $r = -0.55$ ,  $P < 0.01$ , Table 4.6, respectively). This indicates that as more of the herbicide was bound to the soil, it less readily desorbed back into the soil solutions.

Percent herbicide desorption was not significantly correlated with percent clay in any of the LECs.

#### 4.4.2.3 Predicting herbicide behaviour with the soil properties

In the upper LEC sampling points, soil surface pH alone was able to adequately predict the herbicide's  $K_d$  with  $r = -0.50$  ( $K_d = 2.05 - 0.25\text{pH}$ ,  $P < 0.01$ ). Soil organic carbon was not able to significantly predict  $K_d$  in this upper LEC. Combining the soil properties resulted in non-significant  $K_d$  prediction models. Herbicide desorption was well predicted by  $K_d$  alone ( $\% \text{Desorption} = 66.53 - 74.3K_d$ ,  $r = -0.66$ ,  $P < 0.01$ ). While % SOC and pH were each only able to weakly, predict the herbicide desorption ( $\% \text{Desorption} = 61.87 - 10.20\% \text{SOC}$ ,  $r = 0.24$ ,  $P = 0.02$ ;  $\% \text{Desorption} = -88.45 + 18.68\text{pH}$ ,  $r = 0.33$ ,  $P < 0.01$ , respectively). Combining these soil properties, only resulted in non-significant %herbicide desorption prediction models.

For the middle LEC samples,  $K_d$  was weakly predicted by % total carbonates ( $K_d = 0.28 - 0.01\% \text{Total carbonates}$ ,  $r = -0.34$ ,  $P < 0.01$ ) and by soil pH ( $K_d = 1.35 - 0.15\text{pH}$ ,  $r = -0.24$ ,  $P < 0.01$ ). Percent herbicide desorption was moderately predicted by  $K_d$  ( $\% \text{Desorption} = 65.86 - 72.8K_d$ ,  $r = -0.56$ ,  $P < 0.01$ ). With  $K_d$  and percent total carbonates combined, the model marginally improved ( $\% \text{Desorption} = 71.28 - 83.7K_d -$

0.5%Total carbonates,  $r = -0.61$ ,  $P < 0.01$ ). Using other soil properties gave non-significant percent herbicide desorption prediction models.

In the lower LEC, none of the measured properties significantly predicted the herbicide's  $K_d$ . This is important as it may indicate that soil properties which were not measured interfered with the sorption of the 2,4-D onto the soil. Herbicide desorption was adequately predicted when %SOC and pH were combined ( $\%Desorption = 63.19 - 8.77\%SOC - 86.7K_d$ ,  $r = -0.60$ ,  $P < 0.01$ ). Whereas  $K_d$  alone was able to predict the herbicide desorption with  $r = -0.55$  ( $\%Desorption = 70.86 - 78.6K_d$ ,  $P = 0.02$ ).

#### **4.4.3 General Discussion**

The many years of tillage that has occurred on this site has caused the loss of the original topsoil and the subsequent exposure of the less organically-rich-carbonate-rich subsurface soil material (Lindstrom et al. 2000). This has increased the surface soil's pH and has caused the SOC content to decrease relative to an adjacent grassland site. This decrease in soil quality caused the herbicide to be weakly bound to the soil constituents because the average 2,4-D  $K_d$  value was only 0.3 mL/g and, on average, almost 50% of the sorbed herbicide readily desorbed.

This is a concern as the herbicide can readily move within the soil matrix to groundwater since the soil will not be able to sorb the herbicide. As well, any 2,4-D that has sorbed to soil particles, which are then eroded into surface waters, may contaminate these

waterways. This is also a concern since 78 million acres in the United States were devoted to corn production in 1991 (M. Lindstrom 2003, person. comm.) where heavy tillage is often used and thus the soil quality is being degraded. Therefore, when pesticides are applied in these regions that have reduced amounts of SOC to sorb the pesticides, the pesticides will be weakly bound to the soil, and this will negatively affect the groundwater and surface water quality.

The soil and herbicide properties were not uniformly distributed throughout the landscape. Proceeding from the upper to the middle to the lower LECs, the amount of SOC increased, the amount of carbonates decreased, and the surface pH decreased. As a result, the herbicide's  $K_d$  increased from the upper to the middle to the lower LECs. As the pH decreased from the upper LEC to the lower LEC, this caused for more of the herbicide to transform from anionic to the molecular form. Since  $K_d$  and pH were negatively correlated across all points, more 2,4-D sorption onto the soil occurred when the herbicide was in its molecular form.

The herbicide's  $K_d$  was not correlated with %SOC in any of LECs, which was unexpected. With soil samples in the upper and middle LECs that contained average carbonate amounts of 7.5% and 5.6% and average %SOC amounts of 1.01% and 0.97%, respectively, the carbonates could have interfered with the sorption of the 2,4-D onto the SOC in that the carbonates may have sorbed the 2,4-D perhaps preferentially to the SOC. Also, Rao and Davidson (1980) stated that in soils low in organic matter, the correlation

between  $K_d$  and organic matter is less significant when competition with mineral adsorption sites becomes more important. Ionic pesticides can interact with the surface sites of minerals through electrostatic interactions, ion-exchange reactions, or by surface complexation (Brownawell et al. 1990, Schwarzenbach et al.1993, Celis et al. 1996, 1999).

The herbicide's mean  $K_{oc}$  was significantly lower in the upper LEC relative to the two other LECs, thus indicating that the sorptive capacity of the soil organic carbon was not equal across all landscape positions. Perhaps the sorptive capacity of the organic carbon was decreased in the upper LEC because of its large amounts of carbonates that may have interfered with the herbicide binding to the soil organic carbon. Also, the tillage action may not have easily allowed for a stable organic carbon pool to form as the tillage was constantly disrupting the soil's porosity, aggregate stability, and surface crop residues, which are some of the factors that affect SOC formation. The severity of the tillage action was more severe on upper slope positions than on middle and lower LECs. This may have been the cause for SOM quantity differences among the LECs within the landscape.

The measured soil properties were only able to weakly predict  $K_d$  in the upper and middle LECs and none of the soil properties were able to predict  $K_d$  in the lower LEC. A further refinement of landscape units within the lower LEC may lead to better understanding of the correlation between soil properties and  $K_d$ . More than one soil

series each having undergone different solum development processes (e.g. leaching of carbonates or SOC formation) probably existed within each LEC that may have affected the ability to predict the 2,4-D sorption and desorption behaviour. Had the soil series been identified for each sampling location, this might have helped to account for this pedogenic variability and perhaps could have improved some of the correlations between the soil properties and the herbicide sorption and desorption. Other properties, which were not measured in this study, may also have affected the 2,4-D sorption onto the soil constituents.

When classifying this tilled landscape into LECs, it must be noted that the soil properties and topography will change with time. This will have an impact in predicting both the pesticide sorption and desorption by soil within the LECs in the future. As the tillage erosion proceeds, the area affected by tillage erosion becomes increasingly large (Lindstrom et al. 2000). Quine et al. (1994) and Govers et al. (1996) both observed that tillage produced maximum erosion at abrupt convex slope positions, which lead to reduced slope angles and infilling of hollows and a continued reduction of topographic features. This is different than water erosion where the landscape is characterized by increased incision of the concavities and ephemeral gullies and a slow increase in slope angles on convex slope positions occurs (Lindstrom et al. 2000). Since this field has been cultivated for approximately 100 years and annually moldboard plowed for the past 40 years, topographic features have changed to some degree over time (Lindstrom et al. 2000) and will continue to change in the future, if the site is to be tilled in the same manner. This will continue to cause more losses of %SOC and increase the amount of

carbonates in the surface soil, which will, of course, affect pesticide sorption and desorption in the future.

#### 4.5 Summary and Conclusions

The herbicide was found to be weakly bound to the soil constituents due to its low mean value  $K_d$  of 0.3 mL/g, its low average  $K_{oc}$  value of 24.5 mL/g and that, on average, almost 50% of the sorbed herbicide readily desorbed back into soil solutions. These values will affect the 2,4-D leaching and loss at this site in that the herbicide will be able to move readily in and out of the soil matrix. The sorption behaviour of the 2,4-D was not well explained by %SOC. This is contrary to what many other researchers have found, and may indicate that heavy tilled sites (with a degraded soil quality and soil carbonates present in large amounts) behave differently from reduced or zero-tilled sites, with respect to pesticide sorption by soil. The herbicide's  $K_d$  value was moderately affected by the soil pH and carbonates content. Since significant differences in the 2,4-D's  $K_d$  and  $K_{oc}$  values throughout the landscape occurred, and that the %SOC and  $K_{oc}$  were adequately correlated, the herbicide's sorptive behaviour did vary with slope position. More of the sorbed herbicide desorbed in the upper LEC and over all points, herbicide desorption was only predicted by soil pH,  $K_d$ , and  $K_{oc}$ .

## **5. 2,4-D SORPTION AND DESORPTION IN SOIL IN RELATION TO SOIL VARIABILITY AND LANDSCAPE POSITION IN A WESTERN MANITOBA GLACIAL TILL LANDSCAPE**

### **5.1 Abstract**

Soil cores were taken from two hundred and ten points along ten transects that were placed over a gently undulating landscape near Miniota, Manitoba. These cores were then analysed for depth of A horizon, depth of solum, depth of carbonates, %soil organic carbon, pH, %clay, and for the sorption and desorption of the herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) by soil. The landscape was delineated into upper, middle, lower, and depressional landform element complexes (LECs) with the use of a landform description model. The soil cores were also classified into one of three soil series: Angusville, Newdale, and Varcoe. The herbicide was weakly bound to the soil particles as evidenced by its low mean soil-water sorption partitioning coefficient ( $K_d$ ) of 0.6 mL/g, its low mean organic carbon sorption partition coefficient ( $K_{oc}$ ) of 24.5 mL/g, and that large amounts (65.0%) of the sorbed herbicide readily desorbed back into the soil solutions. Multiple linear regression models and correlations between the 2,4-D's  $K_d$  and soil properties revealed that soil organic carbon content, solum depths, depth to carbonates, and depth of A horizon were all significantly correlated with the  $K_d$  values. However,  $K_d$  was most strongly related to soil organic carbon and slope position, where the greatest sorption occurred in the depressional landscape positions, which had the

greatest soil organic carbon amounts. The Angusville soil series contained the most soil organic carbon and sorbed the most 2,4-D relative to the Newdale and Varcoe series. No significant differences in the 2,4-D's  $K_{oc}$  values existed between the LECs, but the Angusville series had a significantly greater median  $K_{oc}$  value relative to the Newdale and Varcoe series. Herbicide desorption did not differ between the LECs, however the Angusville series samples did desorb significantly less of the sorbed herbicide than the other two series. Soil organic carbon content and  $K_d$  were the best soil properties that explained the variation in % 2,4-D desorption within the landscape.

## **5.2 Introduction**

Despite the many recognized benefits that pesticides bring to agricultural production, their presence as contaminants in non-target systems is both undesirable (Khakural et al. 1994) and unsustainable. Identifying soils more vulnerable to pesticide leaching is a key step in developing management practices that safe guard water quality (Novak et al. 1997). This requires an understanding of how pesticides behave in agricultural fields including the variability in pesticide retention by soil across soil series or slope positions within landscapes (Novak et al. 1997).

Pesticide sorption onto and desorption from soil particles are two important processes that influence pesticides' movement in soil. Pesticide sorption onto soil will influence its volatilization, degradation, leaching rates, and uptake by plants and soil fauna (Farenhorst

1998). The amount that pesticides desorb from soil will determine whether the soil is a temporary or a permanent sink for storing pesticides (Graham-Bryce 1981). Pesticide sorption and desorption are both related to soil chemical and physical properties and to the molecular composition of the pesticide (Oliveira Jr. et al. 1999). For example, for pesticides of low polarity and solubility, soil organic matter has been seen as their main adsorbent (Wauchope et al. 2002).

Soil properties will vary spatially within landscapes because of soil forming factors. This variation then influences the distribution of pesticide sorption and desorption within landscapes. For example, soils at bottom slope positions tend to have greater soil organic matter content and greater pesticide sorption capacities than soils in top or middle slope positions (Mallawatantri and Mulla 1992, Vink and Robert 1992, Khakural et al. 1994, Farenhorst et al. 2001).

One common method of quantifying pesticide sorption onto soil is utilizing the soil-water sorption partitioning coefficient,  $K_d$  (Wagenet and Rao 1985, Mallawatantri and Mulla 1992, Coquet and Barriuso 2002, Wauchope et al. 2002). Many research, screening, and management models have been proposed to describe pesticide reactions in soil (Wagenet and Rao 1990) and the outputs of these models are very sensitive to the input value of the soil-water sorption partitioning coefficient (Coquet and Barriuso 2002).

Since soil organic matter is usually the dominant factor in determining the pesticide sorption by soil, the organic carbon sorption partition coefficient ( $K_{oc}$ ) is also used for

quantifying pesticide sorption by soil (Rao and Davidson 1979, Coquet and Barriuso 2002, Wauchope et al. 2002).  $K_{OC}$  values are widely used as measures of the possible movement of pesticides in soils.  $K_{OC}$  is also an important input parameter in fugacity models, which describe the partitioning of pesticides within ecosystems including soil, water, and atmospheric components (Wauchope et al. 2002). The  $K_{OC}$  approach assumes that: (1) herbicides sorb only to SOC (even at low organic C contents), (2) a linear relation exists between  $K_d$  and SOC (even at low organic C contents), and (3) SOC has a continuous sorption capacity (Mallawatantri and Mulla 1992, Green and Karickhoff 1990). Opinions differ about the legitimacy of the  $K_{OC}$  method for environmental applications from support (Chiou et al. 1979) to skepticism (Mingelgrin and Gerstl 1983).

The herbicide, 2,4-Dichlorophenoxyacetic acid (2,4-D) is commonly used to control broadleaf weeds in agricultural crops. This herbicide has been detected in surface water and groundwater samples (Waite et al. 1992, Currie and Williamson 1995, Rawn et al. 1999a). The objectives of this study were to: (1) describe the spatial variability of soil properties, 2,4-D sorption onto soil, and 2,4-D desorption from soil in this gently undulating landscape; and (2) evaluate the LEC and soil series classifications for potential use as predictors of the herbicide's sorption and desorption behaviour.

### 5.3 Materials and Methods

The study site and all of the collected soil samples were first used by Manning (1999) who made available these samples and the collected soil properties' data for this herbicide project. Therefore, the sections describing the study site, experimental design, and soil property analyses are all adapted from Manning (1999).

#### 5.3.1 Study site description

The study site is a gently undulating glacial till landscape situated near Miniota, Manitoba (SE 32-14-25W, Figure 5.1a). This site has been farmed for at least 50 years. In 1978, tillage was reduced to a minimum-till system and a zero-till system was initiated in 1988 along with a cereal-oilseed crop rotation. Soil samples were collected in September 1997. From 1992 to 1997, several different herbicides, including 2,4-D, were applied to the field (Table 5.1).



Figure 5.1a Map of Manitoba indicating study site location

Table 5.1 The herbicides and the active ingredients that have been applied at the Miniota site from 1992-1997 (R. Bell 2000, person. comm.).

<b>Herbicides applied</b>		
<b>Year</b>	<b>Product name(s)</b>	<b>Active Ingredient(s)</b>
1992	Pursuit	Imazethapyr
1993	Triumph Plus	Thifensulfuron methyl
1994	Poast Buctril M	Sethoxydim Bromoxynil and MCPA
1995	Avenge Estaprop	Difenzoquat Dichlorprop and 2,4-D
1996	Treflan	Trifluralin
1997	Assert Refine	Imazamethabenz Thifensulfuron methyl and Tribernuron methyl

Most of the soils in this regional recharge site are Black Chernozems. Fitzmaurice et al. (1999) completed a 1:5000 soil survey over the whole quarter section of the site, which classified the Newdale soil Association into three soil series: Newdale, Angusville, and Varcoe. The Newdale soil series, which are well-drained Orthic Black Chernozems, cover most of the site and mainly occur in middle to upper slope positions (Fitzmaurice et al. 1999). The Angusville soil series, which are classified as Gleyed Eluviated Black Chernozems, are generally found in the lower to toe slope positions and are comprised of imperfectly drained soils (Fitzmaurice et al. 1999). They have strongly leached and eluviated horizons, are sites of net surface water infiltration, and are thicker than the shallower Varcoe series (Fitzmaurice et al. 1999). Soils of the Varcoe series are carbonate-rich Gleyed Rego Black Chernozems and are located near the toe slopes in

close association with the Angusville soils, but are only present in a few locations within the landscape (Fitzmaurice et al. 1999). A more detailed description of these soil series is available in Appendix IB.

### **5.3.2 Experimental design**

Ten adjacent 11 m x 450 m transects were placed over the 5.6 ha site with 21 sampling points in each transect thereby giving a total of 210 sampling points (Figure 5.1b). Points were georeferenced using global position system and demarcated by pinflags. Along each transect, 16 points were uniformly spaced on a regular 30 m basis and the remaining 5 points were dispersed at 15 m intervals between the original 16 points at locations of more noticeable changes in the landscape curvature. The site had classic crest, midslope, and depressional toposequence components that were captured by the ten transects.

For all of the 210 points, soil samples were obtained using a truck-mounted hydraulic coring device. Samples consisted of intact 3.7 cm diameter cores in polyethylene sleeves. All of these cores then had their profiles characterized as described by Agriculture Canada Expert Committee on Soil Science (1987). Depth of the A horizon, depth of solum, and depth to carbonate-rich material were all determined by Manning (1999). With this data and information from Fitzmaurice et al. (1999), each point was classified by soil series (Manning 1999). Only soil samples from the surface Ah or Ahk horizons were used in this herbicide study.

### 5.3.3 Soil property analyses

All samples were first air-dried and ground (<2 mm). Samples were then analysed for soil organic carbon content (%SOC) and pH by Manning (1999). Before the SOC was analysed, inorganic carbon was removed by adding 10 mL of 6N HCl to every sample (Tiessen et al. 1983). Subsequently, the samples were rinsed clean of leftover chlorine with deionized water and suction filtration, and then oven dried at 110°C. A LECO CHN 600 C and N model was used to determine the %SOC, by dry combusting 0.12 g of oven-dried soil (Nelson and Sommers 1982).

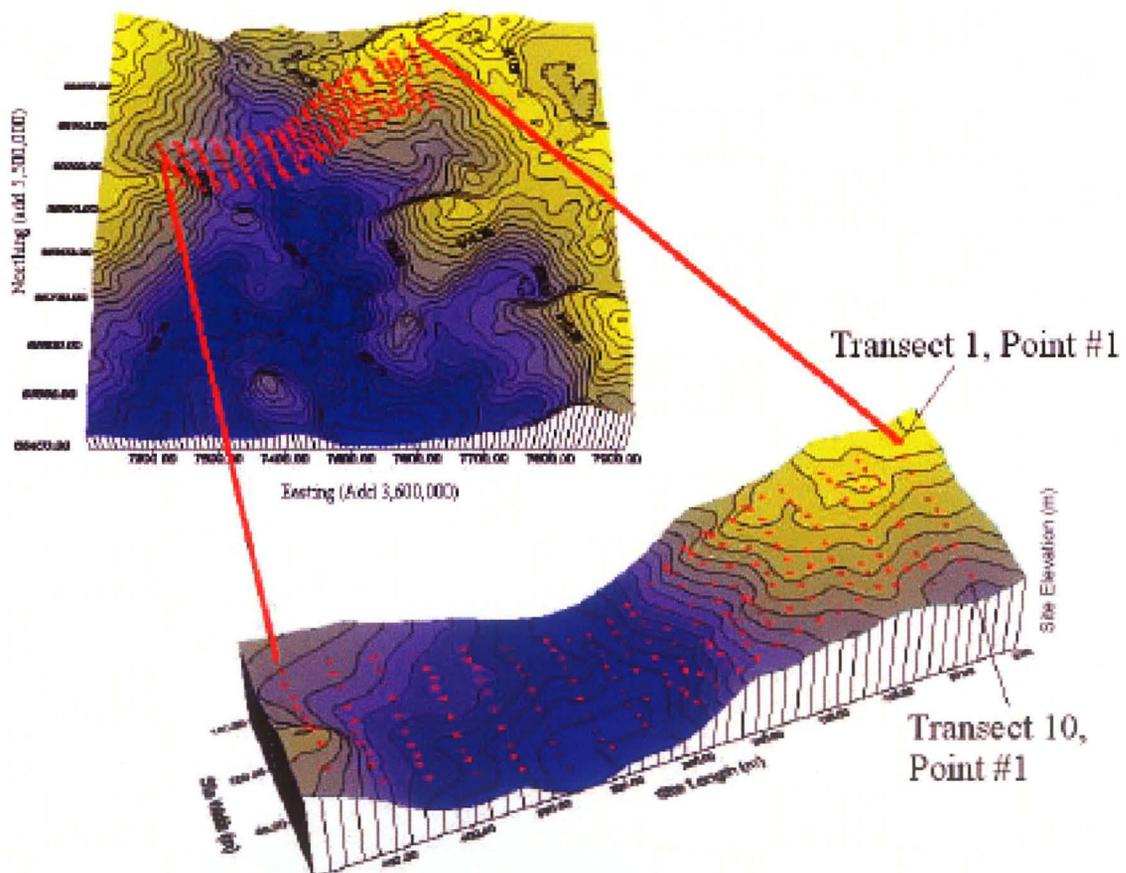


Figure 5.1b Miniota relative site location (SE 32-14-5W), surface morphology and sampling point distributions (adapted from Manning 1999).

Soil pH values were determined by weighing 10 g of soil into 50 mL centrifuge tubes with 20.0 mL of 0.01M CaCl<sub>2</sub>. The samples were then shaken for 30 minutes and the pH was recorded with a glass electrode when the reading stabilized (Hendershot and Lalande 1993). Soil particle size analysis was determined by the pipette method on 51 randomly chosen samples of the 210 cores (Loveland and Whalley 1991).

### **5.3.4 Batch equilibrium experiments**

#### **5.3.4.1 2,4-D sorption onto soil**

The herbicide stock solutions were made by first adding 1.0 mg/L of analytical-grade 2,4-D (95% purity, Sigma Chemical Co., St. Louis, MO.) into a 0.01 M CaCl<sub>2</sub> solution at a pH of 7.1. Approximately 19 Bq/L of [U-ring-<sup>14</sup>C] 2,4-D (99% radiochemical purity; sp. act. 10 mCi/mmol; American Radiolabeled Chemicals Inc. St. Louis, MO.) was then mixed into the stock solution. Herbicide solution (10.0 mL) was added to 5.0 g of air-dried soil into 50 mL Teflon centrifuge tubes. The tubes were then placed in a rotary shaker for 24 hours at room temperature in the dark to reach equilibrium. Following a 24 hour equilibrium period, the soil slurries were vortexed, centrifuged at 10,000 rpm for 10 minutes, and the supernatant was subsampled in 1.0 mL duplicates. Of the 210 soil samples, only 205 were used for the sorption and desorption experiments and each sample was conducted in triplicates. Five samples were not analyzed because there was not enough soil from Manning (1999)'s samples, to determine the sorption and desorption of the herbicide.

Previous batch experiments have shown that 2,4-D sorption on soil occurs rapidly, with most of the herbicide being removed from solution within the first few hours, and that a 24 hour equilibrium period is sufficient to characterize the second phase of slow sorption (Sannino et al. 1997, Wauchope et al. 2002). Preliminary testing revealed that 2,4-D did not adsorb onto the Teflon centrifuge tubes.

A Liquid Scintillation Counter (LSC) (LS 7500 Beckman Instruments, Fullerton, CA) was used to measure the amount of [U-ring-<sup>14</sup>C] 2,4-D with 5.0 mL of ScintiSafe 30% scintillation cocktail (Fisher, Fairlawn NJ.) added to each subsampled (1.0 mL) supernatant. The amount of herbicide sorbed on soil was determined by the difference between the initial and equilibrium herbicide concentrations.

The sorption distribution coefficient,  $K_d$  (mL/g), was calculated assuming linear

partitioning ( $1/n = 1$ ): 
$$K_d = \frac{C_s}{C_e} \quad [1]$$

where  $C_s$  is the concentration of 2,4-D in soil at equilibrium (mg/g) and  $C_e$  is the concentration of 2,4-D in solution at equilibrium (mg/mL). Greater  $K_d$  values denote more pesticide sorption by soil, relative to smaller  $K_d$  values.

The organic carbon sorption partition coefficient ( $K_{oc}$ ) was calculated by normalizing the 2,4-D  $K_d$  values for organic C using the following equation (Novak et al. 1997):

$$K_{oc} = \left( \frac{K_d}{\%SOC} \right) \times 100 \quad [2]$$

#### 5.3.4.2 Percent 2,4-D desorption by soil

After the supernatant was sampled for 2,4-D sorption, the remaining supernatant was removed and replaced by the same amount of a 0.01 M  $CaCl_2$  solution at a pH of 7.1.

The samples were then rotated again for 24 hours in the dark at room temperature to allow equilibrium to reach. After being vortexed and centrifuged at 10,000 rpm for 10 minutes, the supernatant of each sample was subsampled (1.0 mL) in duplicates to quantify the remaining [U-ring- $^{14}C$ ] 2,4-D in solution by the LSC. Percent herbicide desorption (n=205 samples) was calculated on a total [U-ring- $^{14}C$ ] 2,4-D basis:

$$\left( \frac{A}{B} \right) \times 100\% \quad [3]$$

where A is the total amount of [U-ring- $^{14}C$ ] 2,4-D in soil solution following desorption and B is the total amount of [U-ring- $^{14}C$ ] 2,4-D in soil following sorption.

#### 5.3.5 Statistical methods

Using the site's elevation data and the MacMillan and Pettapiece (2000) Landform Description Program, the site was delineated into one of four different Landform Element Complexes (LECs): upper, middle, lower, and depression slope positions. This LEC

classification is based on differences in water distribution and soil development, which are calculated by a landform segmentation model (MacMillan and Pettapiece 2000). The program was run through Microsoft Visual FoxPro version 7 (Microsoft, Redmond, WA. 2001). The computed LECs were then overlaid on the site's digital 3D elevation map using ArcView version 3.2 (ESRI, Redlands CA. 1999) in which the 210 sampling points were assigned their appropriate LEC classification.

Surfer<sup>TM</sup> gridding and contouring software version 6.0.4 (Golden Software, Boulder CO. 1997) with the Kriging method was utilized to produce the 3D data maps. JMP IN version 3.1.5 statistical software program (SAS Institute Inc. 1995) was used to produce the side-by-side quantile boxplots to graphically display the data distributions for each LEC and for each soil series.

Parametric statistical analyses are not valid unless the data follows certain necessities such as having normality and equal variances. Therefore, data were analysed for their normality using the Shapiro-Wilk W test and for equal variances using the Levene's test. Non-normal data were transformed (Table 5.2). Data that did not conform to normality despite various transformation attempts were analysed using the non-parametric multiple median comparison method of the Kruskal-Wallis test as described by Daniel (1990). For the normal data, the Tukey's multiple mean comparison tests were used. All data were then analysed for correlations using the Pearson pairwise correlation coefficient method. Stepwise linear regression analyses using all of the data were also performed. During the regression analyses, all of the independent variables were also checked to

determine if they were related by use of the variance inflation factor test. All statistical tests were done using the SAS statistical software program version 8.01 (SAS Institute Inc. 2000). All statistical significance was set using  $P < 0.05$  as a significance level.

Table 5.2 Assessing if the variables are normalized with or without transformation

Variable	Transformation Type				
	None	$\text{Log}_{10}(x+1)$	$\sqrt{x}$	$x^2$	$\frac{1}{x}$
A horizon Depth	No	Yes	N/A	N/A	N/A
Solum Depth	No	Yes	N/A	N/A	N/A
Depth to Carbonates	No	No	No	No	No
Surface pH	Yes	N/A	N/A	N/A	N/A
%SOC	No	Yes	N/A	N/A	N/A
$K_d$	No	No	Yes	No	No
$K_{oc}$	No	No	No	No	No
%Herbicide Desorption	No	Yes	No	No	No
% Clay	No	No	No	No	No

Legend: No = Data set did not follow a normal distribution  
 Yes = Data set followed a normal distribution and thus was analysed using the Tukey's mean comparison test  
 N/A = transformation was not needed, because data had been normalized

## 5.4 Results and Discussion

### 5.4.1 Soil properties and herbicide behaviour across the landscape

#### 5.4.1.1 The variability of the soil properties and herbicide behaviour

The site's A horizon depth (*A<sub>d</sub>*), varied across the landscape with an average value of 21 cm  $\pm$  9 cm (standard deviation), a median of 19 cm, and ranged from 7 cm to 60 cm (Figure 5.2a). Solum depth (*Solum<sub>d</sub>*) varied from 9 cm to 140 cm with an average value of 37 cm  $\pm$  18 cm and a median of 34 cm (Figure 5.2b). The average depth to carbonates in the soil cores (*CO<sub>3</sub><sub>d</sub>*) was 36 cm  $\pm$  21 cm where the depth varied from 0 cm to 140 cm and its median was 32 cm (Figure 5.2c). Soil surface pH extended from 5.2 to 7.6, its median was 6.3, and its mean was 7.2  $\pm$  0.6 (Figure 5.2d). Soil texture analysis was determined on 51 samples, for which the dominant soil texture was clay loam. The % clay content varied from 2.8% to 52.6%, with a median of 23.8%, and an average of 23.6%  $\pm$  8.8%. The average sand content was 38.3%  $\pm$  8.2% and the mean silt content was 38.1%  $\pm$  10.6%. % Soil organic carbon (%SOC) varied from 1.04% to 4.05%, with a median value of 2.20%, and an average value of 2.31%  $\pm$  0.59% (Figure 5.2e). The herbicide's soil-water partitioning coefficient,  $K_d$ , had an average value of 0.6 mL/g  $\pm$  0.2 mL/g (n = 205), a median of 0.5 mL/g, and ranged from 0.2 mL/g to 1.2 mL/g (Figure 5.2f). These  $K_d$  values are comparable to those obtained by Mallawatantri and Mulla (1992) and Farenhorst et al. (2001) for soils with a similar %SOC. Johnson et al. (1995) studied 2,4-D sorption onto two Arkansas soils, which had a lower % soil organic matter

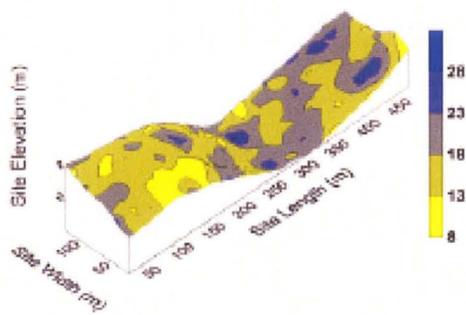


Figure 5.2a The spatial distribution of A horizon depth (cm.)

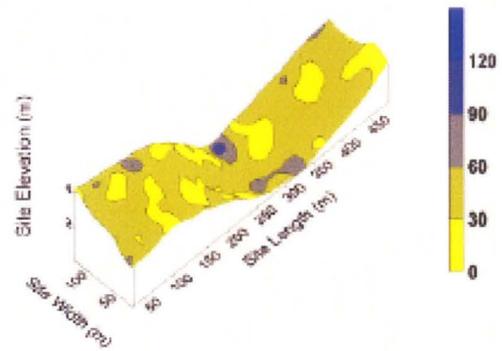


Figure 5.2b The spatial distribution of solum depth (cm.)

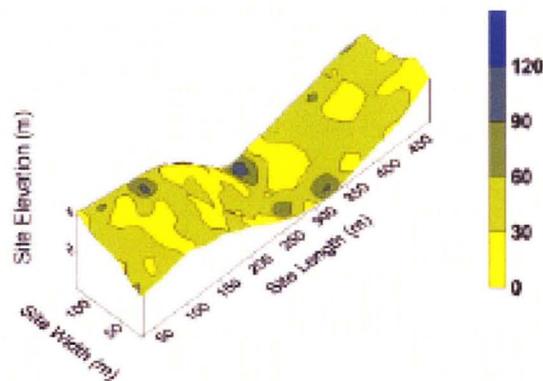


Figure 5.2c The spatial distribution of depth to carbonates (cm.)

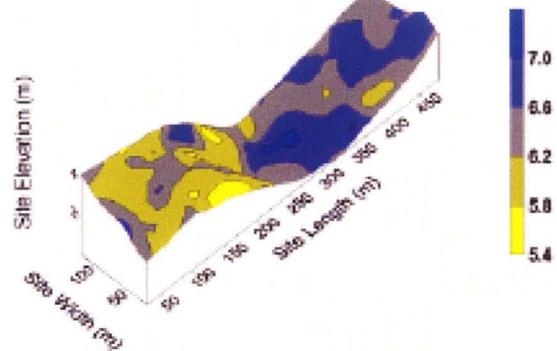


Figure 5.2d The spatial distribution of soil surface pH

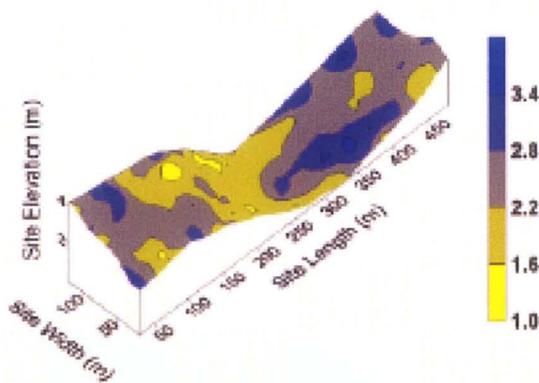


Figure 5.2e The spatial distribution of % soil organic carbon content

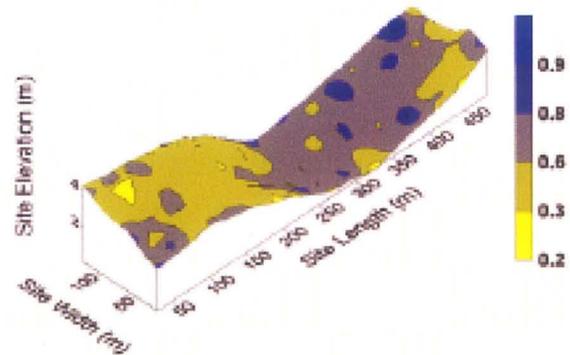


Figure 5.2f The spatial distribution of the herbicide's  $K_d$  (mL/g)

than this study, and obtained 2,4-D  $K_d$  values of 0.59 mL/g and 0.50 mL/g (for two pH 5 soils), and  $K_d$  values of 0.19 mL/g and 0.12 mL/g (for two pH 7 soils).

The herbicide's  $K_{oc}$  had an overall median of 23.7 mL/g, a mean of 24.5 mL/g  $\pm$  7.0 mL/g ( $n = 205$ ) with values that varied from 8.3 mL/g to 57.2 mL/g (Figure 5.2g). This mean  $K_{oc}$  value is similar to the 2,4-D  $K_{oc}$  values reported by both Hamaker and Thompson (1972) and to Rao and Davidson (1980) but is much lower than the 2,4-D  $K_{oc}$  values of Rao and Davidson (1979) who were mentioned earlier in chapter 4.

The practical significance of herbicide sorption depends largely on the extent to which it is reversible (i.e. amount of sorbed herbicide that is released into soil solutions). The amount that the sorbed 2,4-D desorbed back into the soil solutions ranged from 47.8% to 92.2%, had an average value of 65.0 %  $\pm$  8.5%, and had a median of 64.3% ( $n = 205$ ) (Figure 5.2h). This value indicates that over the entire site, the soil was a temporary sink for the herbicide and thus increases its mobility within the soil matrix. Cheah et al. (1997) determined that 2,4-D was more strongly bound to Malaysian soils since only 20% of the sorbed herbicide desorbed from both a sandy loam and a muck soil. Sannino et al. (1997) concluded that about 30% to 40% of the sorbed 2,4-D was easily desorbed, evidently being the only fraction that was weakly bound to the clay particles. The remaining portions of the sorbed 2,4-D could not be removed from the aluminum montmorillonite clay complex, despite many washings with 0.01M  $CaCl_2$  (Sannino et al. 1997).

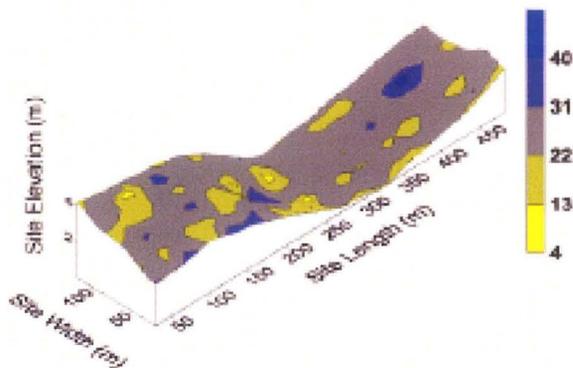


Figure 5.2g The spatial distribution of the herbicide's  $K_{oc}$  (mL/g)

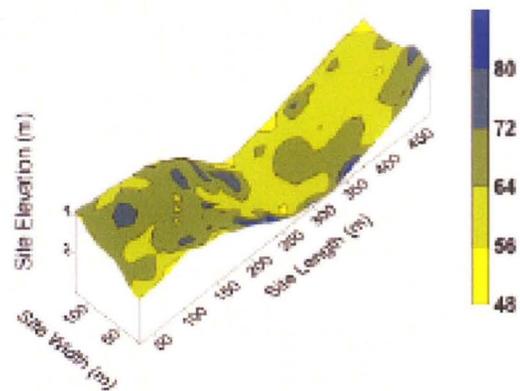


Figure 5.2h The spatial distribution of percent herbicide desorption

#### 5.4.1.2 Correlations between soil properties and the herbicide behaviour

The depth of the A horizon was strongly positively correlated with solum depth ( $r = 0.74$ ,  $P < 0.01$ , Table 5.3). Depth to carbonates were correlated with A horizon depth ( $r = 0.69$ ,  $P < 0.01$ , Table 5.3). Across the entire site, solum depth and the depth to carbonates were very strongly positively correlated ( $r = 0.94$ ,  $P < 0.01$ , Table 5.3) which indicated that the depth of carbonate-rich material often occurred at the surface of the C horizon.

Overall, weak negative correlations existed between pH and depth of solum ( $r = -0.16$ ,  $P = 0.02$ ) and between pH and depth to carbonates ( $r = -0.24$ ,  $P < 0.01$ ) (Table 5.3).

Table 5.3 Pearson pairwise correlation coefficients between all soil properties for all sampling points. (- = not significant at  $P < 0.05$ , = significant at  $P < 0.05$ , \*\* = significant at  $P < 0.01$ )

	%SOC	Surface pH	CO <sub>3</sub> depth	Solum depth	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00								
Surface pH	-	1.00							
CO <sub>3</sub> depth	0.51**	-0.24**	1.00						
Solum depth	0.54**	-0.16 <sup>1</sup>	0.94**	1.00					
Ah depth	0.55**	-	0.69**	0.74**	1.00				
K <sub>d</sub> (n=205)	0.71**	-	0.55**	0.55**	0.54**	1.00			
K <sub>oc</sub> (n=205)	-	-	0.27**	0.24**	0.24**	0.72**	1.00		
%Herbicide desorption (n=205)	-	-	-0.42**	-0.41**	-0.41**	-	-	1.00	
	0.50**					0.78**	0.65**		
%Clay (n=51)	-	-	-	-	-	-	-	-	1.00

Across the site, %SOC was positively correlated with the A horizon depth ( $r = 0.55$ ,  $P < 0.01$ ), depth to carbonates ( $r = 0.51$ ,  $P < 0.01$ ), and with solum depth ( $r = 0.54$ ,  $P < 0.01$ ) (Table 5.3). This was expected, as soil formation processes influencing SOC and A horizon depth are similar and could be the result of the long term differences in crop productivity across the landscape (Solohub 1994). Gollany et al. (1992) also found that SOC decreased as topsoil depth decreased, where the research site was located in South Dakota.

The herbicide's  $K_d$  values had positive correlations with %SOC ( $r = 0.71$ ,  $P < 0.01$ , Figure 5.3), depth to carbonates ( $r = 0.55$ ,  $P < 0.01$ ), and solum depth ( $r = 0.55$ ,  $P < 0.01$ ) (Table 5.3). Since  $K_d$  was positively correlated with these three properties, some spatial dependency then existed among these variables (Figures 5.2b, 5.2c, 5.2e, and 5.2f).

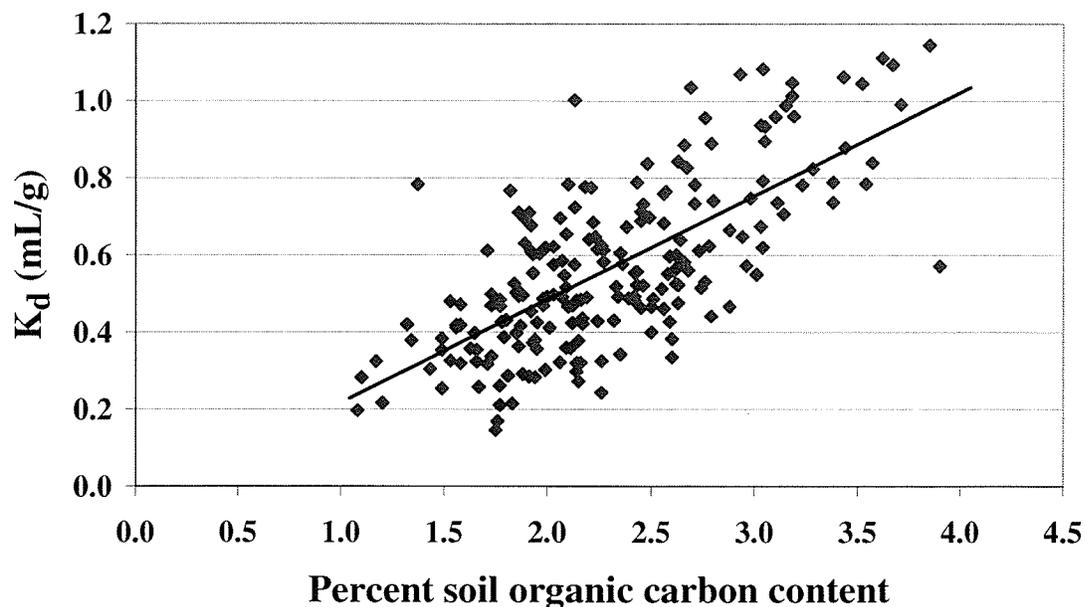


Figure 5.3 Relation between % soil organic carbon and the adsorption partition coefficient ( $K_d$ ) for 2,4-D ( $K_d = -0.05 + 0.27\%SOC$ ,  $r = 0.71$ )

The herbicide's  $K_{OC}$  had weak positive correlations with depth to carbonates ( $r = 0.27$ ,  $P < 0.01$ ), solum depth ( $r = 0.24$ ,  $P < 0.01$ ), and A horizon depth ( $r = 0.24$ ,  $P < 0.01$ ) (Table 5.3). %SOC was not significantly correlated to the herbicide's  $K_{OC}$  (Figure 5.4). This indicates that across all points, the sorptive capacity of the soil organic carbon was not influenced by the soil organic carbon content.  $K_{OC}$  was correlated with % herbicide desorption ( $r = -0.78$ ,  $P < 0.01$ ). Since  $K_d$  and  $K_{OC}$  were strongly correlated, this indicates that SOC was the dominant factor involved in the herbicide sorption. However, their spatial distributions differed from each other (Figures 5.2f and 5.2g), which

indicates that the effects of soil constituents other than organic carbon also influenced the sorption of the 2,4-D.

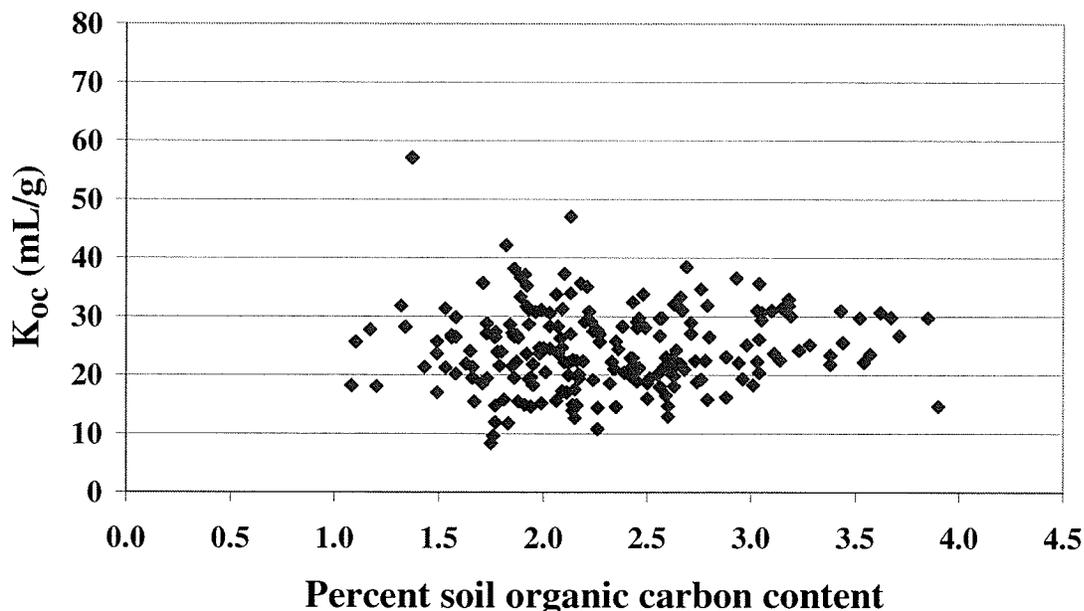


Figure 5.4 Relation between %soil organic carbon and the organic carbon partition coefficient ( $K_{oc}$ ) for 2,4-D ( $K_{oc} = 23.18 + 0.58\%SOC$ ,  $r = 0.0$ )

For all of the soil sampling points combined, the percentage of herbicide desorption was strongly, negatively correlated to the 2,4-D's  $K_d$  ( $r = -0.78$ ,  $P < 0.01$ ) (Table 5.3). This indicates that as more of the herbicide was bound to the soil, it less readily desorbed back into the soil solutions. Johnson et al. (1995) determined that the amount of 2,4-D desorbed increased as the 2,4-D concentration increased. Johnson et al. (1995) suggested that this phenomenon comes from the specific binding sites, which are saturated at higher concentrations and that at these higher herbicide concentrations, weaker sites are responsible for binding the 2,4-D. Cox et al. (1998) determined that the lower the

concentration of imidacloprid in soil solution, the more strongly it sorbed and did not desorb.

Across the entire site, % herbicide desorption had adequate negative correlations with some of the other measured soil properties (Table 5.3). The strongest of these relationships was with %SOC ( $r = -0.50$ ,  $P < 0.01$ , Figure 5.5), followed by depth to carbonates ( $r = -0.42$ ,  $P < 0.01$ ), A horizon depth ( $r = -0.41$ ,  $P < 0.01$ ), and with solum depth ( $r = -0.41$ ,  $P < 0.01$ ).

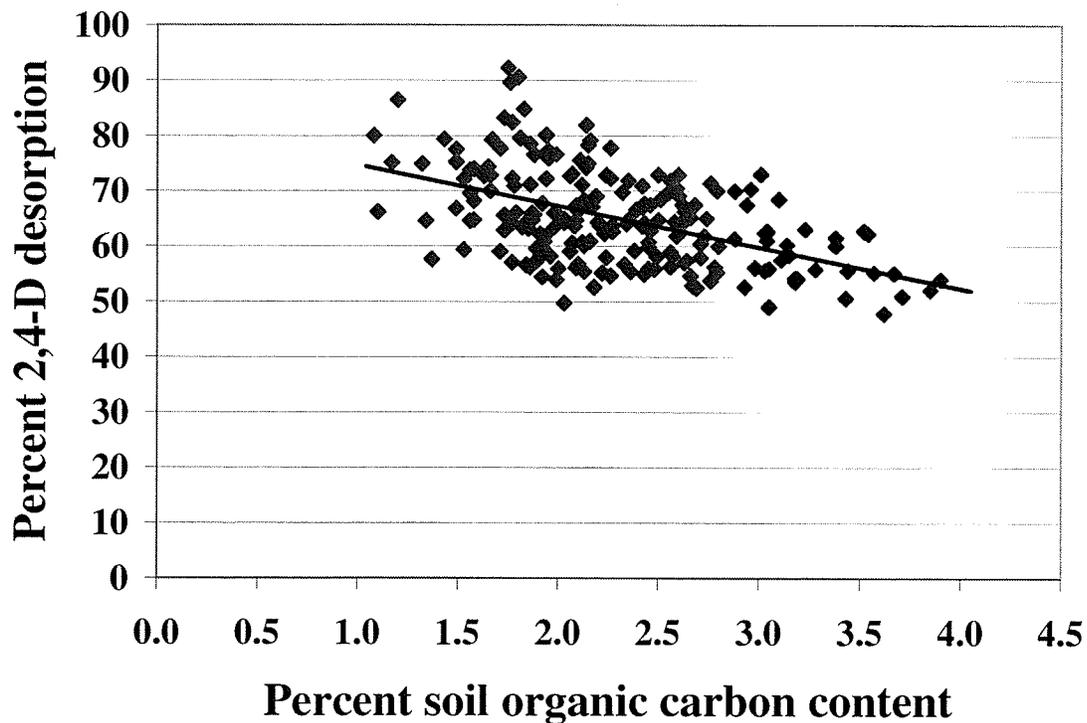


Figure 5.5 Relation between percent soil organic carbon content and percent 2,4-D desorption ( $\%Desorption = 82.10 - 7.44\%SOC$ ,  $r = -0.50$ )

Given the small mean 2,4-D  $K_d$  and  $K_{oc}$  values and that on average large amounts of the herbicide desorbed back into soil solutions, this study demonstrated that the 2,4-D was weakly bound to the soil constituents. Thus, this herbicide is relatively mobile in the soil environment and could represent a threat to water quality.

#### 5.4.1.3 Predicting herbicide behaviour with the soil properties

Utilizing the measured soil properties through stepwise linear regression,  $K_d$  was adequately predicted with A horizon depth, ( $K_d = 0.30 + 0.01A d$ ,  $r = 0.54$ ,  $P < 0.01$ ) solum depth ( $K_d = 0.32 + 0.01Solum d$ ,  $r = 0.55$ ,  $P < 0.01$ ), and depth to carbonates ( $K_d = 0.37 + 0.01CO_3 d$ ,  $r = 0.55$ ,  $P < 0.01$ ). However, %SOC was the main determinant and predictor in the sorption of the herbicide ( $K_d = -0.05 + 0.27\%SOC$ ,  $r = 0.71$ ,  $P < 0.01$ , Figure 5.3). Various other researchers, concluded that 2,4-D sorption onto soil, was best predicted by using %SOC (Grover 1973, Reddy and Gambrell 1987, Mallawantri and Mulla 1992, Johnson et al. 1995, Cheah et al. 1997, Farenhorst et al. 2001). %SOC has also been the main determinant in the sorption of other pesticides by soil, including imidacloprid (Cox et al. 1998), cyanazine (Reddy et al. 1997a), atrazine (Novak et al. 1997), metribuzin (Mallawantri and Mulla 1992), diuron (Mallawantri and Mulla 1992), and triallate (Mallawantri and Mulla 1992).

When other soil properties were each added to %SOC in predicting  $K_d$ , the models were marginally improved. Adding A horizon depth to %SOC ( $K_d = -0.057 + 0.22\%SOC +$

0.01 A  $d$ ) resulted in  $r = 0.74$ , ( $P < 0.01$ ), while adding solum depth to %SOC ( $K_d = -0.042 + 0.22\%SOC + 0.003Solum\ d$ ) gave  $r = 0.74$ , ( $P < 0.01$ ), and also including depth to carbonates ( $K_d = -0.028 + 0.22\%SOC + 0.003CO_3\ d$ ) resulted in  $r = 0.74$  ( $P < 0.01$ ). Combining all of the measured soil properties together did not result in a significantly better prediction of the herbicide's  $K_d$ .

Both pH and %clay had no effect on the 2,4-D's sorption behaviour onto soil (Table 5.3). These two properties individually did not have significant correlations with  $K_d$  and  $K_{oc}$  and including them in regression models with %SOC did not cause for statistical significant increases in the models' ability to better predict  $K_d$ . Mallawatantri and Mulla (1992) also found that soil pH values (ranging from 6.1 to 7.3) had no influence on 2,4-D sorption ( $K_d$  ranging from 0.31 mL/g to 1.27 mL/g). However, Johnson et al. (1995) determined that 2,4-D sorption onto soil was affected by soil pH in that the 2,4-D  $K_d$  values were greater for soils at pH 5 than at pH 7.

Clay minerals in agricultural soils within temperature climates have a net negative charge and thus have an affinity for positively charged chemicals, but very little affinity for negatively charged chemicals (Green and Karickhoff 1990) such as the herbicide 2,4-D in these sorption experiments. A low adsorptive capacity of 2,4-D and other weak acids onto clays, including negative sorption (i.e. repel), has been reported by Weber et al. (1965), Grover (1971), and by Cheah et al. (1997).

Since the herbicide's  $K_d$  could only be predicted at a level of  $r = 0.74$  ( $P < 0.01$ ) other soil properties that were not measured in this study could have attributed to the 2,4-D sorption onto soil. One such property is the soil's cation exchange capacity. Reddy and Gambrell (1987) reported that the cation exchange capacity for 19 soils and sediments helped to explain the extent of 2,4-D sorption behaviour. The pH of the soils and sediments in Reddy and Gambrell's (1987) study varied from 3.4 to 7.8 and this affected the ionic state of the 2,4-D therefore its sorptive behaviour in relation to the cation exchange capacity of the studied materials (Reddy and Gambrell 1987). In other words, the influence of cation exchange capacity will vary depending on whether the 2,4-D molecules are negatively charged, or are in the molecular form, which changes with soil pH.

Another soil property that could influence the 2,4-D sorption onto soil are soil iron oxides onto which 2,4-D has been shown to sorb. Clausen and Fabricius (2001) examined 2,4-D's potential to sorb onto ferrihydrite, goethite, and lepidocrocite. Clausen and Fabricius (2001) found that  $K_d$  values for these iron oxides decreased with increasing pH due to electrostatic interactions between the oxide surface and the 2,4-D in its anionic form. Watson et al. (1973) determined that 2,4-D's sorption behaviour onto goethite was also pH dependent in that maximum sorption occurred near the  $pK_a$  of the herbicide and decreased with increasing pH. In this study, these interactions with iron oxides may have occurred but would most likely be minimal since the pH of the soil samples were well above the 2,4-D  $pK_a$  values.

A horizon depth, solum depth, and depth to carbonates alone each gave similar  $r$  values in predicting the amount of herbicide that desorbed ( $\% \text{Desorption} = 73.13 - 0.4A d$ ,  $r = -0.41$ ,  $P < 0.01$ ;  $\% \text{Desorption} = 72.11 - 0.2Solum d$ ,  $r = -0.41$ ,  $P < 0.01$ ;  $\% \text{Desorption} = 70.94 - 0.2CO_3 d$ ,  $r = -0.42$ ,  $P < 0.01$ , respectively).  $\% \text{SOC}$  alone gave a  $r$  value of  $-0.50$  ( $\% \text{Desorption} = 82.10 - 7.44\% \text{SOC}$ ,  $P < 0.01$ , Figure 5.4). Including other soil properties with  $\% \text{SOC}$  resulted in models that slightly improved predicting  $\% \text{ herbicide desorption}$ . Adding A horizon depth to  $\% \text{SOC}$  gave  $r = -0.52$  ( $\% \text{Desorption} = 82.35 - 5.79\% \text{SOC} - 0.2A d$ ,  $P < 0.01$ ), while including solum depth with  $\% \text{SOC}$  again gave  $r = -0.52$  ( $\% \text{Desorption} = 81.83 - 5.84\% \text{SOC} - 0.02Solum d$ ,  $P < 0.01$ ). Whereas both  $\% \text{SOC}$  and depth to carbonates gave  $r = -0.54$  ( $\% \text{Desorption} = 81.28 - 5.65\% \text{SOC} - 0.1 CO_3 d$ ,  $P < 0.01$ ). However, the herbicide's  $K_d$  was the main property which affected the herbicide's desorption behaviour ( $\% \text{Desorption} = 82.37 - 30.7K_d$ ,  $r = -0.78$ ,  $P < 0.01$ ). Combining all soil properties, resulted in a not significant  $\% \text{ herbicide desorption}$  prediction model.

#### **5.4.2 Soil properties and herbicide sorption and desorption in relation to landform element complexes**

The MacMillan and Pettapiece (2000) Landform Description Program delineated the study site into four different Landform Element Complexes (LECs): upper, middle, lower, and depressional slope positions (Figure 5.6). Upper points are generally water-

shedding areas, middle points are usually water neutral, lower areas are usually water-receiving, and depressional regions are locations where water accumulates (MacMillan and Pettapiece 2000). A total of 51, 72, 73, and 14 sampling points were allocated to the upper, middle, lower, and depressional LECs, which comprised 24%, 34%, 35%, and 7% of the site, respectively.

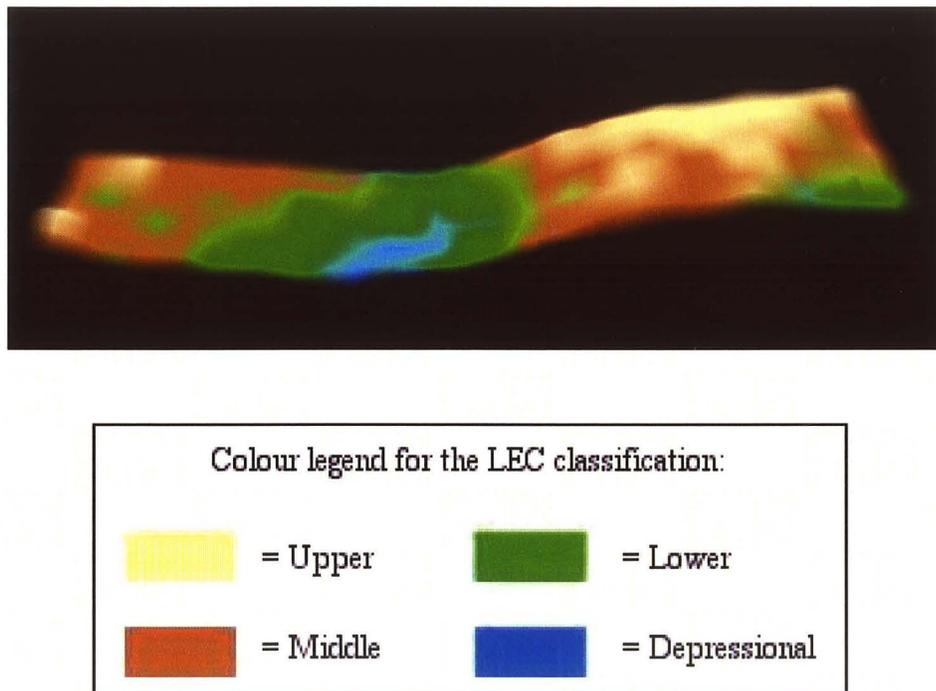


Figure 5.6 The Miniota site's LEC delineations by MacMillan and Pettapiece (2000).

#### 5.4.2.1 The variability of the soil properties and herbicide behaviour

The mean A horizon depths was the same for the upper and middle LECs ( $19 \text{ cm} \pm 8 \text{ cm}$ ,  $19 \pm 7 \text{ cm}$ , respectively) and then increased from the middle to the lower LECs ( $22 \text{ cm} \pm 9 \text{ cm}$ ) to the depressional LEC ( $32 \text{ cm} \pm 12 \text{ cm}$ ) (Figure 5.7a). The depressional LEC had a significantly greater A horizon depth, relative to the other LECs. The median values for

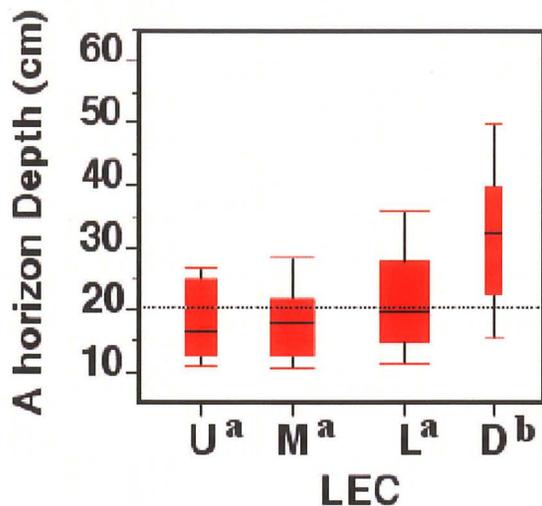


Figure 5.7a A horizon depth distribution by LEC<sup>1</sup>

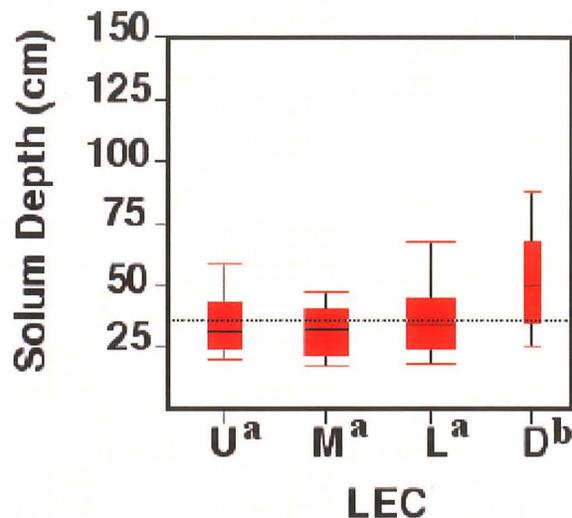


Figure 5.7b Solum depth distribution by LEC<sup>1</sup>

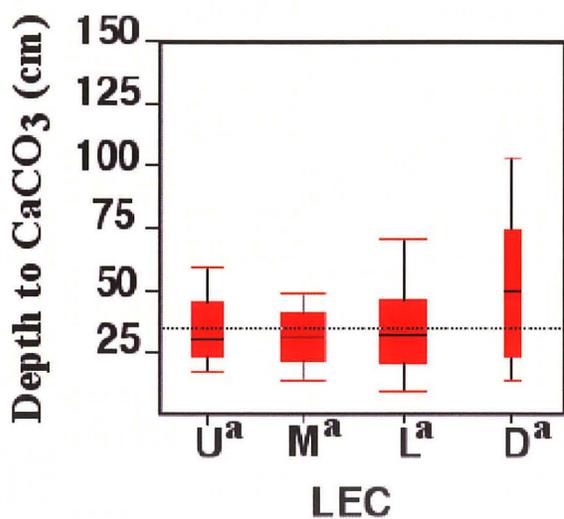


Figure 5.7c Carbonates depth distribution by LEC<sup>1</sup>

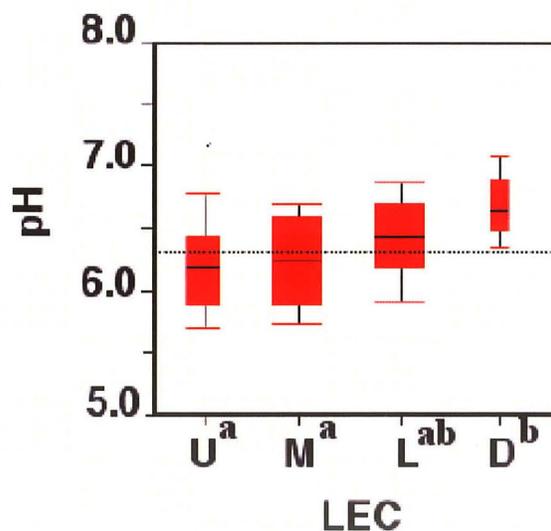


Figure 5.7d Soil surface pH distribution by LEC<sup>1</sup>

1. These quantile boxes graphically display the distribution of the each variable across the LECs. The groups' medians are shown as a line across the middle of each figure and the quartiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) are at its ends (SAS Institute Inc. 1995). The 10<sup>th</sup> and 90<sup>th</sup> quantiles are shown as lines above and below the box (SAS Institute Inc. 1995). The same letters beside the LECs indicates that the means (or medians for CO<sub>3</sub> d only) of the distributions are significantly different at P < 0.05. The larger the sample size, the wider are the quantile boxes.

the A horizon depths across the LECs were 17 cm (upper), 18 cm (middle), 20 cm (lower), and 33 cm (depressional). The mean solum depths decreased from the upper (37 cm  $\pm$  18 cm) to the middle LECs (33 cm  $\pm$  12 cm) and then increased from the middle to the lower LECs (38 cm  $\pm$  21 cm) to the depressional LEC (54 cm  $\pm$  21 cm) (Figure 5.7b). The median values for solum depth across the LECs were 32 cm (upper), 33 cm (middle), 35 cm (lower), and 50 cm (depressional). The depressional LEC had significantly greater values for the solum depth, relative to the other LECs. The results for A horizon and solum depth may suggest that soil from upper slope positions had been wind and water eroded and deposited down slope.

The mean values for the depth to carbonates across the LECs were 36 cm  $\pm$  22 cm, 32 cm  $\pm$  14 cm, 36 cm  $\pm$  24 cm, and 52 cm  $\pm$  30 cm for the upper, middle, lower, and depressional LECs, respectively. The median depth values to carbonate-rich material increased from the upper (30 cm) to the middle (32 cm) to the lower (32 cm) to the depressional LECs (50 cm); however, no significant differences were found between these values (Figure 5.7c).

Other researchers have also found that the A horizon depth, solum depth, and depth to carbonates vary spatially in a similar fashion to this study. For a research site in California, Miller et al. (1988), found that knoll and shoulder slope positions were characterized by shallow soils (<50 cm), while deeper soils (>100 cm) were mostly located on foot and toeslope positions. A horizon thickness was also thinnest at the knolls and thicker at back and footslope positions (Miller et al. 1988). In southern

Saskatchewan, Pennock and de Jong (1990) found the smallest mean A horizon depth in shoulder and backslope elements with convex-slope positions, while greater A horizon mean depths were in footslope elements with concave across-slope positions. Pennock and de Jong (1990) also determined that the distribution of depth to carbonates within this landscape was similar to the A horizon distribution.

The mean pH values varied across the LECs in the order of upper ( $6.5 \pm 0.5$ ) > middle ( $6.3 \pm 0.4$ ) < lower ( $6.6 \pm 0.4$ ) < depressional ( $6.7 \pm 0.2$ ) LECs (Figure 5.7d). The mean pH in the depressional LEC was significantly greater than the mean pH in the upper, middle, and lower LECs. The median pH values also increased in the similar order: 6.2 (upper), = 6.2 (middle), < 6.4 (lower), < 6.6 (depressional). Soils were less acidic in the depressional LEC, which suggests that the surface pH has been altered either by cultivation or by hydrological reversal (Manning 1999). As the surface pH values were related with the hydrologic progression from well to imperfectly drained soils, perhaps since cultivation, the eluvial soils now receive bases from below via capillary action, from a shallow water table (Manning 1999).

The % clay content in soil did not significantly vary among the different LECs. The mean %clay amounts were  $23.6\% \pm 7.9\%$ ,  $24.1\% \pm 7.1\%$ ,  $23.6\% \pm 10.9\%$ , and  $23.2\% \pm 9.5\%$  for the upper, middle, lower, and depressional LECs, respectively. The median %clay values across the upper, middle, lower, and depressional LECs were 22.5%, 26.6%, 24.2%, and 23.8%, respectively (Figure 5.7e). Novak et al. (1997) determined that %clay content increased from upper slope positions to depressional slope positions in an Iowa site.

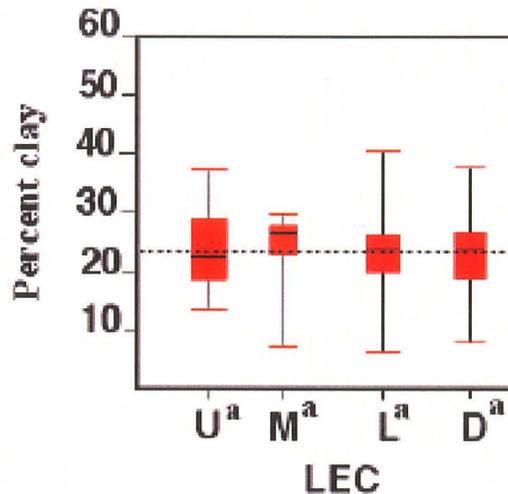


Figure 5.7e The percent clay content's distribution by LEC<sup>1</sup>.

1. These quantile boxes graphically display the distribution of the each variable across the LECs. The groups' medians are shown as a line across the middle of each figure and the quartiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) are at its ends (SAS Institute Inc. 1995). The 10<sup>th</sup> and 90<sup>th</sup> quantiles are shown as lines above and below the box (SAS Institute Inc. 1995). The same letters beside the LECs indicates that medians of the distributions are not significantly different at  $P < 0.05$  using the Kruskal-Wallis median comparison test (Daniel 1990). The larger the sample size, the wider are the quantile boxes.

The mean values for %SOC increased from the upper LEC ( $2.05\% \pm 0.58\%$ ) to the middle LEC ( $2.16\% \pm 0.50\%$ ) to the lower LEC ( $2.48\% \pm 0.51\%$ ) to the depressional LEC ( $3.05\% \pm 0.51\%$ ) (Figure 5.7f). The mean %SOC amounts were significantly greater for the lower and depressional LECs than for the upper and middle LECs. The median %SOC values also increased across the LECs from 1.98% (upper) to 2.11% (middle) to 2.46% (lower) to 3.05% (depressional). This spatial variation in the %SOC is a result of differences in soil formation, depositional and erosional processes across the site. As well, the observed increase of %SOC in lower slope positions maybe due to the increased biomass production (Ellis 1938). Miller et al. (1988), Mallawatantri and Mulla

(1992), and Novak (1999) all reported a similar spatial distribution of soil organic carbon to this study.

The herbicide's average  $K_d$  values increased in the order of upper LEC ( $0.5 \text{ mL/g} \pm 0.2 \text{ mL/g}$ ) < middle ( $0.6 \text{ mL/g} \pm 0.2 \text{ mL/g}$ ) = lower ( $0.6 \text{ mL/g} \pm 0.2 \text{ mL/g}$ ) < depressional LEC ( $0.8 \text{ mL/g} \pm 0.2 \text{ mL/g}$ ) (Figure 5.7g). However, only the mean  $K_d$  of the depressional LEC was significantly greater than  $K_d$  values in the other LECs. The median  $K_d$  values were  $0.5 \text{ mL/g}$  (upper),  $0.5 \text{ mL/g}$  (middle),  $0.6 \text{ mL/g}$  (lower), and  $0.8 \text{ mL/g}$  (depressional). Both %SOC and  $K_d$  increased in the order of the upper < middle < lower < depressional LECs. Significantly greater amounts of %SOC were in the depressional LEC, therefore this area also showed significantly greater 2,4-D sorption by soil relative to the other LECs.

Mallawatantri and Mulla (1992) had a similar spatial distribution of 2,4-D sorption within a Washington State site. Novak et al. (1997) determined that atrazine  $K_d$  values were less in shoulder than depressional positions within an Iowa landscape. In the Miniota, Iowa and Washington State sites, increased amounts of SOC from upper to lower landscape positions occurred, which appeared to have accounted for the increased herbicide sorption by soils.

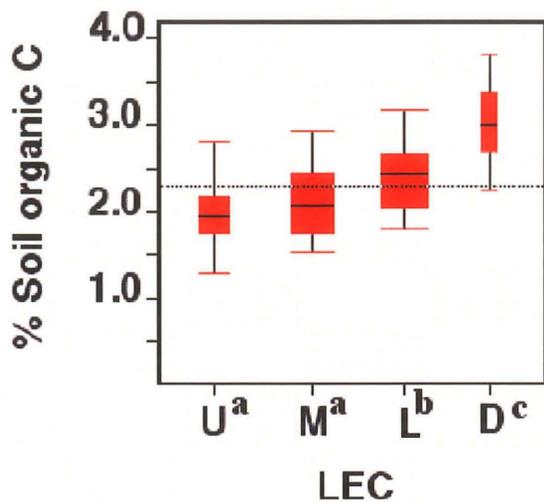


Figure 5.7f Percent soil organic carbon distribution by LEC<sup>1</sup>

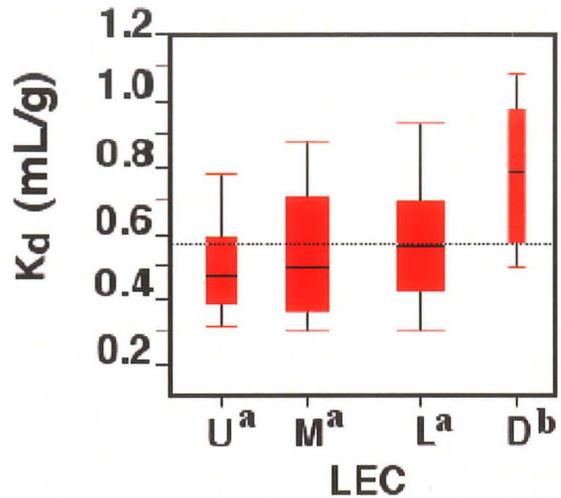


Figure 5.7g The herbicide's  $K_d$  distribution by LEC<sup>1</sup>

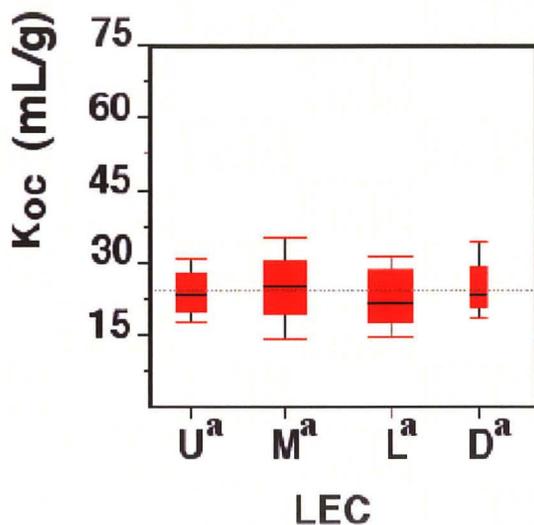


Figure 5.7h The herbicide's  $K_{oc}$  distribution by LEC<sup>1</sup>

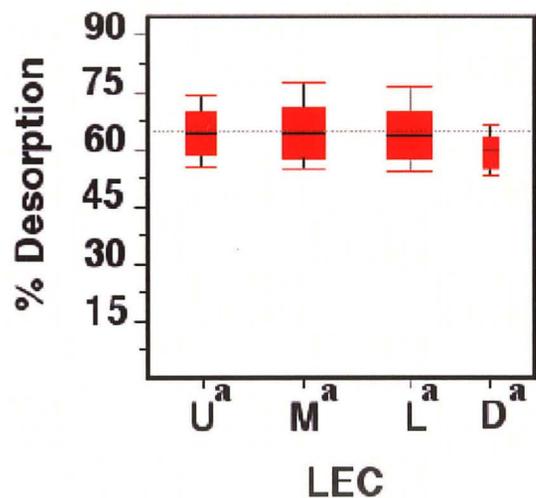


Figure 5.7i The percent herbicide desorption distribution by LEC<sup>1</sup>

1. These quantile boxes graphically display the distribution of the each variable across the LECs. The groups' medians are shown as a line across the middle of each figure and the quartiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) are at its ends (SAS Institute Inc. 1995). The 10<sup>th</sup> and 90<sup>th</sup> quantiles are shown as lines above and below the box (SAS Institute Inc. 1995). The same letters beside the LECs indicates that the means (or medians for  $K_{oc}$  only) of the distributions are not significantly different at  $P < 0.05$ . The larger the sample size, the wider are the quantile boxes.

The means for the herbicide's  $K_{OC}$  across the LECs were 24.5 mL/g  $\pm$  5.3 mL/g (upper), 25.7 mL/g  $\pm$  8.4 mL/g (middle), 23.2 mL/g  $\pm$  6.5 mL/g (lower), and 25.7 mL/g  $\pm$  5.4 mL/g (depressional). The herbicide's  $K_{OC}$  did not significantly differ amongst the LECs as the  $K_{OC}$  median values for the LECs were 24.0 mL/g (upper), 25.7 mL/g (middle), 22.3 mL/g (lower), and 23.7 mL/g (depressional) (Figure 5.7h). These results indicate that the amount of 2,4-D sorbed per unit of organic carbon was independent of the amount of soil organic carbon present (Figure 5.4). Also, it appears that 2,4-D sorption by soil was not influenced by differences in soil organic matter quality across the LECs, or alternatively there was no difference in the soil organic matter quality across the landscape.

For the Miniota site, %SOC was always the dominant factor in explaining the sorption behaviour of the herbicide across the landscape. Novak et al. (1997) studied the spatial distribution of  $K_{OC}$  for atrazine and found that  $K_{OC}$  was lower in the upper slopes versus the depressional slope positions. This was attributed to increasing soil organic carbon and clay contents, as well as greater herbicide sorption in the lower landscape positions (Novak et al. 1997).

For Miniota, the mean % amounts of herbicide desorption slightly decreased from the upper (65.6%  $\pm$  8.1%) to the middle (65.4 %  $\pm$  9.1%) to the lower (65.0%  $\pm$  8.6%) to the depressional (60.0%  $\pm$  5.2%) LECs, but were not statistically different (Figure 5.7i). The median values for percent herbicide desorption for the LECs were 65.0% (upper), 64.7% (middle), 64.3% (lower), and 60.1% (depressional). Therefore, despite spatial differences

in the soil properties and herbicide sorption across the landscape, the amount of herbicide desorption did not differ with landscape position. At all landscape positions the herbicide was weakly bound to the soil constituents and was a temporary sink for the herbicide. These results suggest that 2,4-D can leach through the soil surface quite easily.

#### **5.4.2.2 Correlations between soil parameters and the herbicide behaviour**

For each LEC, the depth of the A horizon was positively correlated with solum depth, but the strength of correlation varied across the LECs (Tables 5.4, 5.5, 5.6, 5.7). The  $r$  values ranged from 0.34 ( $P < 0.01$ ) in the middle LEC (Table 5.5) to 0.75 ( $P < 0.01$ ) (Table 5.6) in the lower LEC. A horizon depth was also well correlated with depth to carbonates in all LECs (Tables 5.4, 5.5, 5.6, 5.7), where the best correlation was  $r = 0.72$  ( $P < 0.01$ ) in the lower LEC (Table 5.6). Solum depth and depth to carbonates were very strongly related within every LEC, suggesting that carbonates were predominantly found at the surface of the C horizon.

Soil surface pH was correlated to depth to carbonates, in the upper and lower LECs with  $r = -0.35$  ( $P = 0.01$ ) (Table 5.4) and  $r = -0.44$  ( $P < 0.01$ ) (Table 5.6), respectively. Only in the lower and depressional LECs was pH correlated to solum depth with  $r = -0.36$  ( $P < 0.01$ ) (Table 5.6) and  $r = -0.56$  ( $P = 0.04$ ) (Table 5.7), respectively. %SOC had similar correlation strengths with both solum depth and depth to carbonates, with  $r$  values around

Table 5.4 Pearson pairwise correlation coefficients between all soil properties for the upper LEC points only (n=51).  
 (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	CO <sub>3</sub> depth	Solum depth	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00								
Surface pH	-	1.00							
CO <sub>3</sub> depth	0.52**	-0.35*	1.00						
Solum depth	0.55**	-	0.93**	1.00					
Ah depth	-	-	0.65**	0.34**	1.00				
K <sub>d</sub> (n=48)	0.81**	-	0.70**	0.70**	-	1.00			
K <sub>oc</sub> (n=48)	-	-	0.48**	0.45**	-	0.59**	1.00		
%Herbicide desorption (n=48)	-	-	-0.45**	-0.47**	-0.35*	-	-	1.00	
%Clay (n=14)	0.52**	-	-	-	-	0.72**	0.53**	-	1.00

Table 5.5 Pearson pairwise correlation coefficients between all soil properties for the middle LEC points only (n=72). (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	CO <sub>3</sub> depth	Solum depth	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00								
Surface pH	-	1.00							
CO <sub>3</sub> depth	0.54**	-	1.00						
Solum depth	0.51**	-	0.88**	1.00					
Ah depth	0.41**	-	0.69**	0.70**	1.00				
K <sub>d</sub> (n=71)	0.64**	-	0.49**	0.43**	0.46**	1.00			
K <sub>oc</sub> (n=71)	-	-	-	-	0.28*	0.76**	1.00		
%Herbicide desorption (n=71)	-	-	-0.41**	-0.25*	-0.33*	-	-	1.00	
%Clay (n=11)	0.45**	-	-	-	-	0.74**	0.62**	-	1.00
	-	-	-	-	-	-	-	-	-

Table 5.6 Pearson pairwise correlation coefficients between all soil properties for the lower LEC points only (n=71). (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	CO <sub>3</sub> depth	Solum Depth	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00								
Surface pH	-0.29*	1.00							
CO <sub>3</sub> depth	0.51**	-0.44**	1.00						
Solum depth	0.53**	-0.36**	0.97**	1.00					
Ah depth	0.47**	-	0.72**	0.75**	1.00				
K <sub>d</sub>	0.67**	-0.35**	0.54**	0.52**	0.52**	1.00			
K <sub>oc</sub>	-	-0.26*	0.34**	0.31*	0.34**	0.83**	1.00		
%Herbicide desorption	-0.53**	-	-0.46**	-0.47**	-0.48**	-0.78**	-0.98**	1.00	
%Clay (n=14)	-	-	-	-	-	-	-	-	1.00

Table 5.7 Pearson pairwise correlation coefficients between all soil properties for the depressional LEC points only (n=14). (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	CO <sub>3</sub> depth	Solum depth	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00								
Surface pH	-0.69*	1.00							
CO <sub>3</sub> depth	-	-	1.00						
Solum depth	-	-0.56*	0.95**	1.00					
Ah depth	0.67*	-	0.58*	0.63*	1.00				
K <sub>d</sub> (n=13)	0.67*	-0.60*	-	0.57*	-	1.00			
K <sub>oc</sub> (n=13)	-	-	-	-	-	0.85**	1.00		
%Herbicide desorption (n=13)	-	-	-	-	-	-0.82**	-0.82**	1.00	
%Clay (n=12)	-	-	-	-	-	-	-	-	1.00

0.53 ( $P < 0.01$ ) except for the depressional LEC where the correlations were not significant.

The herbicide's  $K_d$  was strongly correlated to %SOC in all of the LECs with  $r$  values that ranged from 0.64 ( $P < 0.01$ ) in the middle LEC (Table 5.5) to 0.81 ( $P < 0.01$ ) in the upper LEC (Table 5.4). The herbicide's  $K_d$  was correlated with solum depth within each LEC, with  $r$  values ranging from 0.43 in the middle LEC ( $P < 0.01$ , Table 5.5) to 0.70 in the upper LEC ( $P < 0.01$ , Table 5.4).  $K_d$  was also adequately correlated with depth to carbonates, except in the depressional LEC. In addition,  $K_d$  was weakly correlated to A horizon depth in the middle and lower LECs ( $r = 0.46$ ,  $P < 0.01$  and  $r = 0.52$ ,  $P < 0.01$ , respectively). These results suggest that 2,4-D sorption was moderately correlated with the variability of the soil's leaching regime and organic material buildup within the Miniota landscape. An increased leaching in soils, increases the depth to carbonates as well as both solum and A horizon depths. Organic matter additions to soil also increases A horizon depth, as well as %SOC over time which will in turn increase the herbicide's  $K_d$ .

In the lower and depressional LECs,  $K_d$  was correlated to soil pH with  $r = -0.35$  ( $P < 0.01$ ) and  $r = -0.60$  ( $P = 0.03$ ), respectively. This suggests that an increased pH caused the herbicide molecules to lose more protons, thus becoming anionic, and reducing the herbicide's sorption ability. With each unit increase of soil pH, the amount of herbicide that is in the anionic form increases tenfold. Thus, with more of the herbicide in the anionic form in the depressional LEC, this was indicative that 2,4-D sorption should

occur preferentially as molecular form whereas the anionic form had less affinity for the soil surfaces.

The  $K_{OC}$  was strongly related to  $K_d$  in all LECs with  $r$  values that increased from the upper ( $r = 0.59$ ,  $P < 0.01$ ) to the middle ( $r = 0.76$ ,  $P < 0.01$ ) to the lower ( $r = 0.83$ ,  $P < 0.01$ ) to the depressional LECs ( $r = 0.85$ ,  $P < 0.01$ ) (Tables 5.4, 5.5, 5.6, and 5.7). %SOC and  $K_{OC}$  were not correlated in any of the LECs. As such, the sorptive capacity of the %SOC did not vary with different soil organic carbon contents.

Percent herbicide desorption was more strongly correlated with  $K_d$  than with any other variable for the upper, ( $r = -0.72$ ,  $P < 0.01$ ), middle ( $r = -0.74$ ,  $P < 0.01$ ), and depressional LECs ( $r = -0.82$ ,  $P < 0.01$ ). For the lower LEC, % herbicide desorption was better correlated with  $K_{OC}$  ( $r = -0.98$ ,  $P < 0.01$ ), but the correlation between % herbicide desorption and  $K_d$  was also very good ( $r = -0.78$ ,  $P < 0.01$ ) (Table 5.6). Percent herbicide desorption was also moderately correlated with  $K_{OC}$  in the other LECs. As well, % herbicide desorption was moderately correlated to %SOC in the upper ( $r = -0.52$ ,  $P < 0.01$ ), the middle ( $r = -0.45$ ,  $P < 0.01$ ) and in the lower ( $r = -0.53$ ,  $P < 0.01$ ) LECs (Tables 5.4, 5.5, and 5.6).

### 5.4.2.3 Predicting herbicide behaviour with the soil properties

Although %SOC was the dominant factor affecting the sorption of 2,4-D onto soil, its ability to predict the 2,4-D's  $K_d$  varied amongst the landscape positions. In the upper LEC, %SOC best predicted  $K_d$  with  $r = 0.81$  ( $K_d = -0.04 + 0.27\%SOC$ ,  $P < 0.01$ ) but %SOC predicted  $K_d$  to a lesser extent in the middle ( $K_d = -0.05 + 0.28\%SOC$ ,  $r = 0.64$ ,  $P < 0.01$ ), lower ( $K_d = -0.12 + 0.28\%SOC$ ,  $r = 0.67$ ,  $P < 0.01$ ), and depressional ( $K_d = -0.20 + 0.32\%SOC$ ,  $r = 0.67$ ,  $P = 0.01$ ) LECs. The differences in  $r$  values among the LECs suggest that additional soil properties were involved in the sorption of 2,4-D by soil. This could include soil properties that were not measured such as the soil's cation exchange capacity and iron oxides.

Combining %SOC with other soil properties data slightly improved the prediction models for  $K_d$ . For example, in the upper LEC, %SOC and depth to carbonates combined predicted  $K_d$  with a  $r$  value of 0.87 ( $K_d = -0.029 + 0.003CO_3 d + 0.20\%SOC$ ,  $P = 0.01$ ), while in the middle and lower LECs, %SOC and the A horizon depth together predicted  $K_d$  with  $r$  values of 0.68 and 0.71 ( $K_d = -0.10 + 0.24\%SOC + 0.1A d$ ,  $P = 0.02$ ;  $K_d = -0.11 + 0.23\%SOC + 0.01A d$ ,  $P = 0.01$ , respectively). However, for each LEC, when additional soil properties were combined to predict  $K_d$ , the models were not significantly better.

%SOC alone was able to adequately predict % herbicide desorption in both in the upper (%Desorption =  $81.03 - 7.47\%SOC$ ,  $P = 0.01$ ) and in the lower (%Desorption =  $86.88 - 8.83\%SOC$ ,  $P < 0.01$ ) LECs with r values of -0.53 and in the middle LEC (%Desorption =  $82.26 - 8.23\%SOC$ ,  $r = -0.46$ ,  $P < 0.01$ ). In the depressional LEC, none of the measured soil properties were able to produce a significant prediction model for % herbicide desorption. For every LEC, when other soil properties were combined to predict the amount of herbicide desorbed, the models produced were all insignificant.

#### **5.4.3 Soil properties and herbicide sorption and desorption by soil in relation to soil series**

Soil profile descriptions for each of the 210 points revealed that 151 were classified as the Newdale series, 38 as the Angusville series, and 21 as the Varcoe series. The distribution of the soil series within the site's four landform element complexes (MacMillan and Pettapiece 2000) is given in Table 5.8. This LEC classification showed that the three soil series were found within the landscape positions that were expected based on the fieldwork by Fitzmaurice et al. (1999) (i.e. 68% of the Newdale series points were located within the upper and middle LECs, Table 5.8).

Table 5.8 The distribution of the soil series within the landform element complexes

Soil Series	Landform Element Complex				Total
	Upper	Middle	Lower	Depressional	
Angusville	9 (24%) <sup>a</sup>	9 (24%)	14 (37%)	6 (15%)	38
Newdale	42 (28%)	61 (40%)	45 (30%)	3 (2%)	151
Varcoe	0 (0%)	2 (10%)	14 (67%)	5 (23%)	21
<b>Total</b>	<b>51</b>	<b>72</b>	<b>73</b>	<b>14</b>	<b>210</b>

a. The numbers in parentheses indicate the percentage distribution of the soil series within each LEC.

#### 5.4.3.1 The variability of the soil properties and herbicide behaviour

The mean depths of the A horizon increased significantly from the Newdale series (18 cm  $\pm$  6 cm) to the Varcoe series (22 cm  $\pm$  8 cm) to the Angusville series (33 cm  $\pm$  10 cm) (Figure 5.8a). The median A horizon depths were 32 cm (Angusville), 16 cm (Newdale), and 20 cm (Varcoe). This increase in A horizon depth corresponded to the progression from well drained (Newdale) to imperfectly drained soils (Varcoe and Angusville) (Manning 1999). As well, an increase in the A horizon depth is due to the accumulation of organic matter to the mineral soil (Pennock and de Jong 1990).

Both solum depth and depth to carbonates increased significantly in the order of Varcoe < Newdale < Angusville series (Figures 5.8b and 5.8c). The mean values for solum depth were 63 cm  $\pm$  21 cm for the Angusville series, 32 cm  $\pm$  11 cm for the Newdale series, and

25 cm  $\pm$  10 cm for the Varcoe series. The median values for solum depth were 59 cm, 30 cm, and 23 cm for the Angusville, Newdale and Varcoe soil series, respectively. The average values for the depth to carbonates were 67 cm  $\pm$  23 cm for the Angusville series, 30 cm  $\pm$  13 cm for the Newdale series, and 16 cm  $\pm$  10 cm for the Varcoe series. The median values for the depth to carbonate-rich materials were 61 cm (Angusville), 29 cm (Newdale), and 19 cm (Varcoe).

This increase in solum depth and depth to carbonates across the soil series can be attributed to the soil series' leaching potential and landscape position. Solum depth and depth to carbonate-rich materials are both a function of downward leaching of water and permeability of the parent material, and are frequently related to the amount of convergence in the landscape (Manning 1999). Also, depth to carbonates is generally greater at landscape positions where the net downward infiltration is large and sustained, such as in lower and depressional areas (Manning 1999). Since 20 of the 38 Angusville series' points were located in the lower and depressional LECs, therefore this soil had significantly greater solum and carbonates depths, relative to the other two soil series. This agrees well with results reported earlier where the depressional LEC had the greatest solum depth, which is where the Angusville is the dominant series present. While, the Varcoe soils with a weak leaching regime, and no B horizon development had the shallowest overall mean values for depth to carbonates and solum depth (Manning 1999).

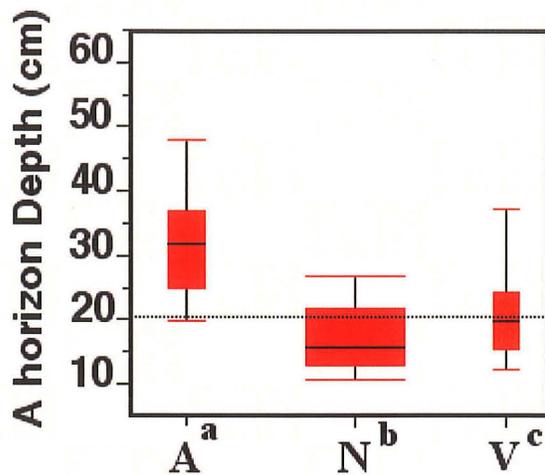


Figure 5.8a A horizon depth distribution by soil series<sup>1</sup>

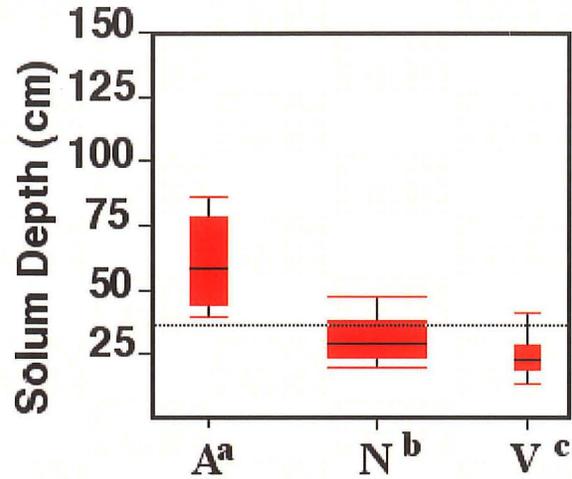


Figure 5.8b Solum depth distribution by soil series<sup>1</sup>

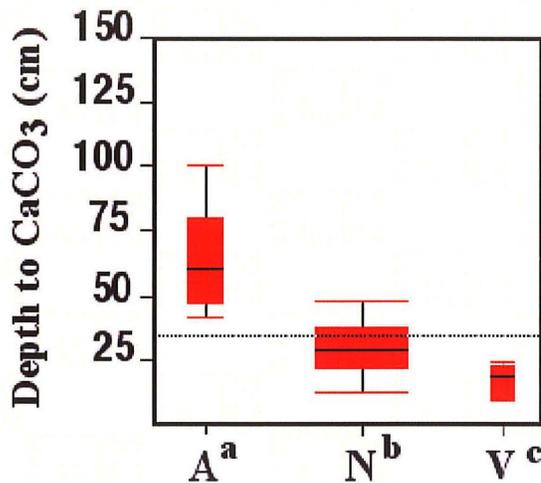


Figure 5.8c Depth to carbonates distribution by soil series<sup>1</sup>

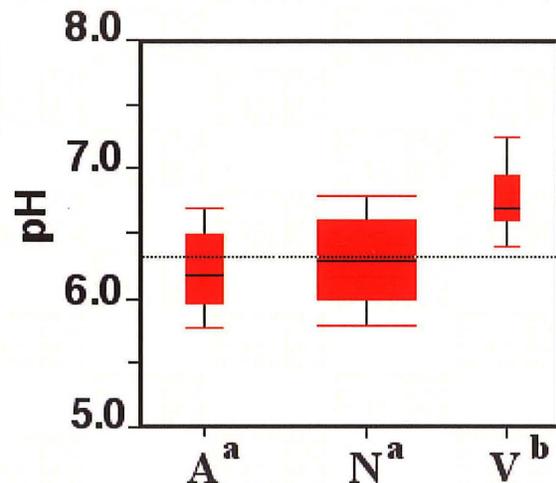


Figure 5.8d Soil surface pH distribution by soil series<sup>1</sup>

1. These quantile boxes graphically display the distribution of the each variable across the LECs. The groups' medians are shown as a line across the middle of each figure and the quartiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) are at its ends (SAS Institute Inc. 1995). The 10<sup>th</sup> and 90<sup>th</sup> quantiles are shown as lines above and below the box (SAS Institute Inc. 1995). Different letters beside the LECs indicates that the means (or medians for depth to carbonates only) of the distributions are significantly different at  $P < 0.05$ . The larger the sample size, the wider are the quantile boxes.

The mean surface pH values were  $6.3 \pm 0.3$ ,  $6.4 \pm 0.4$ , and  $6.8 \pm 0.3$  for the Angusville, Newdale, and Varcoe series, respectively (Figure 5.8d). The median pH values were 6.2, 6.3, and 6.6 for the Angusville, Newdale and Varcoe series, respectively. This pH difference was statistically significant in that the Varcoe soils, with carbonates closest to the soil surface, were the most alkaline soils. The pH values were generally lower in the more strongly leached soils.

The percent clay content mean values were  $23.7\% \pm 8.6\%$  (Angusville),  $24.7\% \pm 8.8\%$  (Newdale), and  $19.2\% \pm 8.8\%$  (Varcoe) (Figure 5.8e). The clay content did not differ significantly among the site's three soil series with median values of 20.8% for the

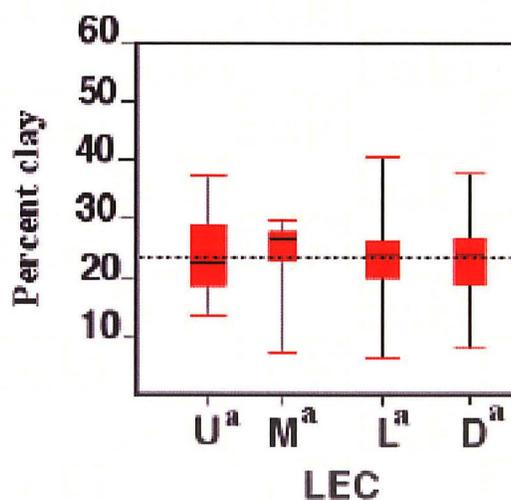


Figure 5.8e The distribution of percent clay content by soil series<sup>1</sup>.

1: These quantile boxes graphically display the distribution of the each variable across the LECs. The groups' medians are shown as a line across the middle of each figure and the quartiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) are at its ends (SAS Institute Inc. 1995). The 10<sup>th</sup> and 90<sup>th</sup> quantiles are shown as lines above and below the box (SAS Institute Inc. 1995). The same letters beside the LECs indicates that medians of the distributions are not significantly different at  $P < 0.05$  using the Kruskal-Wallis median comparison test (Daniel 1990). The larger the sample sizes, the wider are the quantile boxes.

Angusville series, 24.8% for the Newdale series, and 23.7% for the Varcoe series. The %SOC increased from the Newdale ( $2.16\% \pm 0.50\%$ ) < Varcoe ( $2.35\% \pm 0.60\%$ ) < Angusville ( $2.85\% \pm 0.56\%$ ) soil series, where the %SOC was significantly greatest in the Angusville series (Figure 5.8f). The median %SOC values across the soil series were 3.00% (Angusville), 2.11% (Newdale), and 2.27% (Varcoe). For a site near Minnedosa, Manitoba, Bergstrom et al. (2001) found a similar trend with these same soil series. The relation between %SOC and soil series can be explained by factors such as drainage and landscape position. These factors will control the variation in plant material accumulation, differences in carbon and nitrogen mineralization, and soil erosional and deposition processes (Gregorich and Anderson 1985). Poorly drained soils with relatively poor aerations (i.e. the Angusville soil series) usually contain more organic matter than their better drained equivalents (i.e. the Newdale and Varcoe soil series). In addition, organic material from the upper and middle slope positions may have been eroded and transported downslope to the lower and depressional slope positions.

The Angusville soil series had significantly greater values for both  $K_d$  ( $0.8 \text{ mL/g} \pm 0.2 \text{ mL/g}$ ) and  $K_{oc}$  ( $28.0 \text{ mL/g}$ ) relative to the other two soil series (Figures 5.8g and 5.8h). This was expected because the Angusville series contained the most SOC relative to the other two series. The Varcoe soils' mean  $K_d$  value ( $0.5 \text{ mL/g} \pm 0.2 \text{ mL/g}$ ) was similar to that for the Newdale soils' mean  $K_d$  value ( $0.5 \text{ mL/g} \pm 0.2 \text{ mL/g}$ ). The median  $K_d$  values were  $0.8 \text{ mL/g}$  (Angusville),  $0.5 \text{ mL/g}$  (Newdale), and  $0.5 \text{ mL/g}$  (Varcoe). The Varcoe

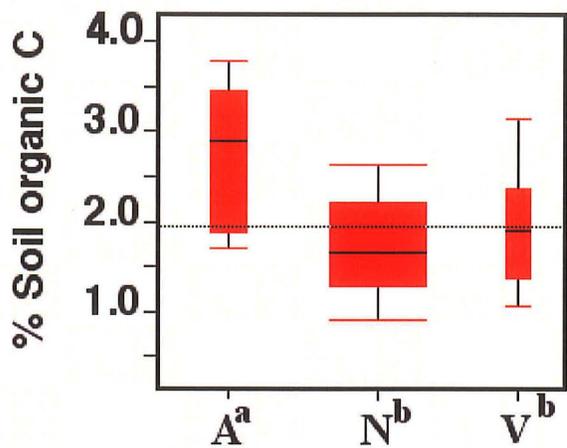


Figure 5.8f Soil organic carbon distribution by soil series<sup>1</sup>

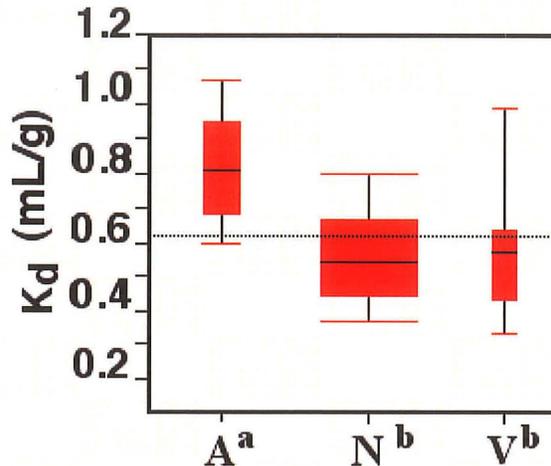


Figure 5.8g The herbicide's  $K_d$  distribution by soil series<sup>1</sup>

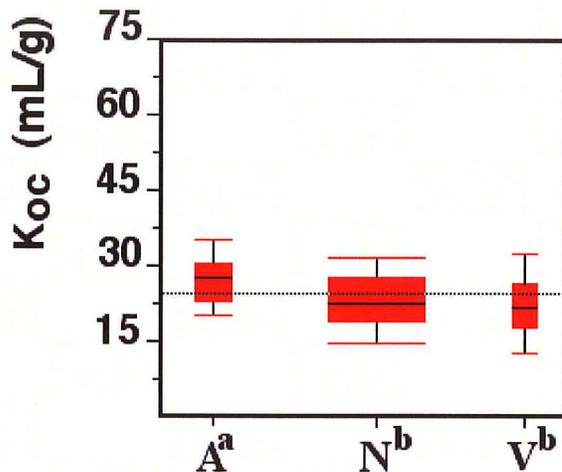


Figure 5.8h The herbicide's  $K_{oc}$  distribution by soil series<sup>1</sup>

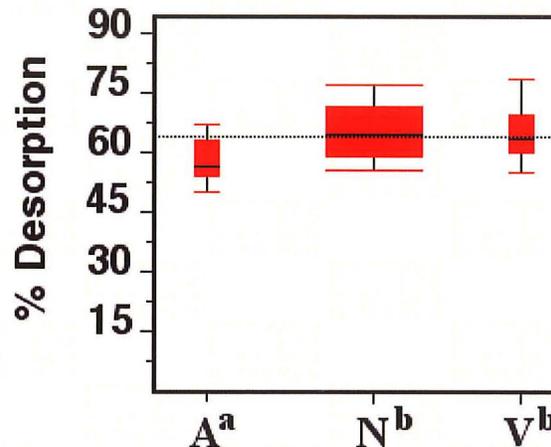


Figure 5.8i Percent herbicide distribution by soil series<sup>1</sup>

1. These quantile boxes graphically display the distribution of the each variable across the LECs. The groups' medians are shown as a line across the middle of each figure and the quartiles (25<sup>th</sup> and 75<sup>th</sup> percentiles) are at its ends (SAS Institute 1995). The 10<sup>th</sup> and 90<sup>th</sup> quantiles are shown as lines above and below the box (SAS Institute Inc. 1995). Same letters beside the LECs indicates that the means (or medians for  $K_{oc}$  only)

of the distributions are not significantly different at  $P < 0.05$ . A is the Angusville soil series, N is the Newdale soil series, and V is the Varcoe soil series. The larger the sample size, the wider are the quantile boxes.

and Newdale series both had similar median  $K_{OC}$  values of 22.2 mL/g and 22.9 mL/g, respectively. This narrow range of  $K_{OC}$  values indicates that the soil organic carbon content was the most important variable in explaining the herbicide sorption by soil.

The Newdale series and the Varcoe series had similar mean amounts of % herbicide desorption with values of  $66.4\% \pm 8.5\%$  and  $66.0\% \pm 8.3\%$ , respectively (Figure 5.8i), but the Angusville series desorbed significantly less of the sorbed herbicide ( $59.1\% \pm 6.4\%$ ). The median values for the percent herbicide desorption were 57.2% (Angusville), 65.2% (Newdale) and 64.2% (Varcoe). Therefore soils with greater soil organic carbon content, which had greater  $K_d$  and  $K_{OC}$  values, released less of the sorbed herbicide back into the soil solutions.

#### **5.4.3.2 Correlations between soil properties and the herbicide behaviour**

The A horizon depth had moderate to good correlations with solum depth and with depth to carbonates across all soil series (Tables 5.9, 5.10, 5.11). Solum depth and depth to carbonates were strongly correlated within all of the series but the strongest correlation was in the Angusville series ( $r = 0.94$ ,  $P < 0.01$ , Table 5.9).

Only in the Varcoe soil series was surface pH correlated with depth to carbonates ( $r = -0.65$ ,  $P < 0.01$ , Table 5.11). In contrast, the Angusville soils, which were characterized by deep solums and deeper depths to carbonates, were more acidic and the soil pH values were not correlated with depth to carbonates. The site's %SOC was significantly

Table 5.9 Pearson pairwise correlation coefficients between all soil properties for the Angusville soil series points only (n=38). (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	CO <sub>3</sub> depth	Solum depth	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00								
Surface pH	-	1.00							
CO <sub>3</sub> depth	-	-	1.00						
Solum depth	-	-	0.94**	1.00					
Ah depth	-	0.40*	0.62**	0.58**	1.00				
K <sub>d</sub>	0.63**	-	-	-	-	1.00			
K <sub>oc</sub>	-	-	-	-	-	0.59**	1.00		
%Herbicide desorption	-0.39*	-	-	-	-	-0.77**	-0.54**	1.00	
%Clay (n=11)	-	-	-	-	-	-	-	-	1.00

Table 5.10 Pearson pairwise correlation coefficients between all soil properties for the Newdale soil series points only (n=151). (- = not significant at  $P < 0.05$ , \* = significant at  $P < 0.05$ , \*\* = significant at  $P < 0.01$ )

	%SOC	Surface pH	CO <sub>3</sub> depth	Solum depth	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00								
Surface pH	-	1.00							
CO <sub>3</sub> depth	0.47**	-	1.00						
Solum depth	0.47**	-	0.87**	1.00					
Ah depth	0.44**	0.22*	0.49**	0.60**	1.00				
K <sub>d</sub> (n=147)	0.64**	-	0.45**	0.41**	0.34**	1.00			
K <sub>oc</sub> (n=147)	-	-	0.19*	-	-	0.73**	1.00		
%Herbicide desorption (n=147)	-	-	-0.41**	-0.31**	-0.29**	-	-	1.00	
%Clay (n=32)	0.41**	-	-	-	-	0.73**	0.63**	-	1.00

Table 5.11 Pearson pairwise correlation coefficients between all soil properties for the Varcoe soil series points only (n=21). (- = not significant at P < 0.05, \* = significant at P < 0.05, \*\* = significant at P < 0.01)

	%SOC	Surface pH	CO <sub>3</sub> depth	Solum depth	Ah depth	K <sub>d</sub>	K <sub>oc</sub>	%Herbicide desorption	%Clay
%SOC	1.00								
Surface pH	-	1.00							
CO <sub>3</sub> depth	0.49**	-0.65**	1.00						
Solum depth	0.65**	-	0.66**	1.00					
Ah depth	0.72**	-	0.68**	0.75**	1.00				
K <sub>d</sub> (n=20)	0.53*	-	-	0.59*	0.60**	1.00			
K <sub>oc</sub> (n=20)	-	-	-	-	-	0.84**	1.00		
%Herbicide desorption (n=20)	-0.54*	-	-	-0.61**	-0.52*	-0.86**	-0.74**	1.00	
%Clay (n=8)	-	-	-	-	-	-	-	-	1.00

correlated with A horizon depth in the Newdale and in the Varcoe series ( $r = 0.44$ ,  $P < 0.01$  and  $r = 0.72$ ,  $P < 0.01$ , respectively).

The herbicide's  $K_d$  was positively correlated with the %SOC content across the Angusville, Newdale, and Varcoe soil series with  $r = 0.63$  ( $P = 0.01$ ),  $r = 0.65$  ( $P < 0.01$ ), and  $r = 0.53$  ( $P = 0.01$ ), respectively (Tables 5.9, 5.10, and 5.11). As well the herbicide's  $K_d$  was strongly correlated with  $K_{oc}$  in the Angusville, Newdale, and Varcoe soil series with  $r = 0.59$  ( $P < 0.01$ ),  $r = 0.73$  ( $P < 0.01$ ), and  $r = 0.84$  ( $P < 0.01$ ), respectively.

Herbicide desorption was adequately to strongly negatively correlated to both the herbicide's  $K_d$  and  $K_{oc}$  in all of the series. The strongest of these relationships was in the Varcoe series with  $r = -0.86$  ( $P < 0.01$ ) for  $K_d$  and  $r = -0.74$  ( $P < 0.01$ ) for  $K_{oc}$  (Table 5.11). Percent 2,4-D desorption was weakly negatively correlated to %SOC in the Angusville and Newdale series  $r = -0.39$  ( $P = 0.02$ ) and  $r = -0.41$  ( $P < 0.01$ ), respectively. In the Varcoe series %SOC was more strongly related to % 2,4-D desorption ( $r = -0.54$ ,  $P = 0.02$ ), relative to the other two series. This indicates that with more %SOC, the 2,4-D molecules were more strongly bound to the soil constituents, therefore less of the sorbed herbicide desorbed.

#### 5.4.3.3 Predicting herbicide behaviour with the soil properties

In the Angusville series, the only significant soil property that was able to predict  $K_d$  was %SOC ( $K_d = 0.15 + 0.22\%SOC$ ,  $r = 0.63$ ,  $P < 0.01$ ). When other measured soil properties were combined with %SOC, the models did not significantly improve.

In the Newdale series, %SOC again was the dominant property in explaining the herbicide's sorption by soil ( $K_d = 0.002 + 0.24\%SOC$ ,  $r = 0.64$ ,  $P < 0.01$ ). Also, depth to carbonates ( $K_d = 0.32 + 0.01CO_3 d$ ,  $r = 0.45$ ,  $P < 0.01$ ), solum depth ( $K_d = 0.29 + 0.01Solum d$ ,  $r = 0.41$ ,  $P < 0.01$ ), and A horizon depth ( $K_d = 0.33 + 0.01A d$ ,  $r = 0.34$ ,  $P < 0.01$ ) were each able to predict  $K_d$  but with lower  $r$  values than %SOC. For the Newdale series, depth to carbonates and %SOC combined gave a  $r$  value of 0.66 ( $K_d = -0.01 + 0.20\%SOC + 0.003CO_3 d$ ,  $P < 0.01$ ). Including all soil properties did not improve the prediction of  $K_d$ .

In the Varcoe series, the depth of the A horizon was able to best predict  $K_d$  with  $r = 0.60$  ( $K_d = 0.15 + 0.02 A d$ ,  $P < 0.01$ ). The herbicide's  $K_d$  was also moderately predicted by %SOC and solum depth ( $K_d = -0.03 + 0.25\%SOC$ ,  $r = 0.54$ ,  $P < 0.01$ ;  $K_d = 0.19 + 0.01Solum d$ ,  $r = 0.59$ ,  $P < 0.01$ , respectively). With all of the measured soil properties placed together, a non-significant  $K_d$  prediction model was produced.

In each soil series,  $K_d$  alone was the property that most strongly predicted the percent herbicide desorption. In the Angusville series, the prediction model was  $\% \text{Desorption} = 78.45 - 24.8 K_d$  ( $r = -0.77$ ,  $P < 0.01$ ), while in the Newdale series the strength of prediction was slightly less with  $r = -0.73$  ( $\% \text{Desorption} = 83.59 - 33.4 K_d$ ,  $P < 0.01$ ). The strongest prediction model was in the Varcoe series ( $\% \text{Desorption} = 83.72 - 33.5 K_d$ ,  $r = -0.86$ ,  $P < 0.01$ ). SOC content alone was also able to predict the herbicide's desorption in each of the soil series, but the regression equations again had different strengths of prediction (Angusville:  $\% \text{Desorption} = 71.62 - 4.40\% \text{SOC}$ ,  $r = -0.39$ ,  $P = 0.02$ ; Newdale:  $\% \text{Desorption} = 81.35 - 6.92\% \text{SOC}$ ,  $r = -0.41$ ,  $P < 0.01$ ; Varcoe:  $\% \text{Desorption} = 87.65 - 9.55\% \text{SOC}$ ,  $r = -0.54$ ,  $P = 0.02$ ). Including additional soil properties with  $\% \text{SOC}$  resulted in non-significant prediction models for both the Angusville and Varcoe series. However, in the Newdale series adding depth to carbonates to  $\% \text{SOC}$  slightly improved the prediction to  $r = 0.48$  ( $\% \text{Desorption} = 82.20 - 4.77\% \text{SOC} - 0.2CO_3 d$ ,  $P < 0.01$ ). Also, in the Varcoe points, solum depth alone gave a slightly better  $\% \text{ herbicide desorption prediction than } \% \text{SOC alone, with } r = -0.61$  ( $\% \text{Desorption} = 79.34 - 0.6Solum d$ ,  $P < 0.01$ ).

#### **5.4.4 General Discussion**

For understanding the spatial variability of the soil properties and herbicide behaviour within the landscape, the 210 sampling points were classified into one of four LECs or into one of three soil series. Classifying this landscape into LECs, based on the relatively

new method from MacMillan and Pettapiece (2000) is innovative as no other herbicide study has used this landscape classification system. This LEC method offered an alternative to soil series classification for the basis of a sampling and/or estimation procedure. The LEC method involved less intense field and lab work than when the samples were classified to the appropriate soil series.

Upon examining these two classifications systems, spatial differences in the landscape properties emerged, which affected the correlations and regression prediction models of the herbicide's sorptive and desorptive behaviour. This is partly because in each LEC more than one soil series was present (Table 5.8). One difference between these two classification methods was that the LEC method showed no significant differences for depth to carbonates,  $K_{OC}$ , and percent herbicide desorption. When the data were sorted by soil series, the Angusville series had significantly greater values for these three properties.

However, when predicting the herbicide's  $K_d$  by %SOC alone through regression equations, different models and coefficient of correlations were determined in the two classification methods. These  $r$  values from the  $K_d$  regression prediction models varied from 0.64 ( $P < 0.01$ ) to 0.81 ( $P < 0.01$ ) in the LECs, whereas by the soil series, the  $r$  values varied from 0.54 ( $P < 0.01$ ) to 0.64 ( $P < 0.01$ ). However, all of the LEC and some of the soil series  $K_d$  prediction models had negative y-axis intercepts which means that these models may not accurately estimate  $K_d$  values at low %SOC contents.

While predicting the percent herbicide desorption, with just %SOC, the prediction models from the soil series gave r values that ranged from  $-0.39$  ( $P = 0.02$ ) to  $-0.54$  ( $P = 0.02$ ). The regression herbicide desorption prediction LEC models gave r values that extended from  $-0.46$  ( $P < 0.01$ ) to  $-0.53$  ( $P < 0.01$ ), however no significant model could be achieved in the depressional LEC. Therefore, the LEC method is a suitable alternative to soil series classification in predicting the 2,4-D's behaviour and in displaying the spatial variability of the soil properties.

Novak et al. (1997) examined the spatial variability of atrazine sorption in relation to soil properties that were classified by soil series and by landscape position in an Iowa site. Novak et al. (1997) determined through regression equations that landscape position was more accurate in representing the spatial variations within the field than by soil series.

### **5.5 Summary and Conclusions**

The herbicide was weakly bound to the soil constituents, due to its low mean value  $K_d$  of  $0.6$  mL/g, its low average  $K_{oc}$  value of  $24.5$  mL/g, and because on average  $65.0\%$  of the herbicide readily desorbed back into soil solutions. The herbicide's  $K_d$  was most strongly related to soil organic carbon and slope position, where the greatest sorption occurred in the depressional LEC, which had the greatest soil organic carbon amounts. The Angusville soil series was found to contain the greatest values for A horizon depth, solum depth, depth to carbonates, and soil organic carbon. Soil in this series sorbed the most 2,4-D relative to the Newdale and Varcoe series. No significant differences in the 2,4-D's  $K_{oc}$  values were found between the LECs, but the Angusville series had a

significantly greater median  $K_{OC}$  value relative to the other series. Herbicide desorption did not differ between the LECs however, the Angusville series desorbed significantly less of the sorbed herbicide than the other two series. Little spatial variability in the amounts of herbicide desorption occurred amongst the LECs, in which  $K_d$  and %SOC were the best properties that explained for its variation.

This study has implications for uses in 2,4-D fate modeling and in landscape based agricultural practices. Groundwater contamination of the 2,4-D may still be at risk in upper slope positions where the herbicide sorption was the least. Any sorbed 2,4-D may still be transported away from the target area via wind or water erosion. These eroded soil particles could then be moved to surface waters and cause contamination.

## **6. GENERAL DISCUSSION**

### **6.1 Comparison of the Miniota and Morris study sites**

#### **6.1.1 Soil properties and herbicide behaviour**

The Miniota soils had shallower A horizon depths, a more acidic pH, fewer carbonates, and more SOC than the Morris soils. These differences in the soil properties between the two sites were because of site differences in climate, topography, vegetation, and tillage management. Both sites are in grassland regions, have a similar glacial till parent material, and have had some of the same agricultural crops grown. However, in the Miniota region, the average annual precipitation is around 46.0 cm (Smith et al. 1998) while at Morris the average annual precipitation is around 61.0 cm (United States Department of Agriculture and National Resources Conservation Service 2000a). This increased precipitation amount at Morris could have caused for increased leaching of organic materials through the soil matrix, thereby contributing to its deeper A horizon depths relative to Miniota. As well, the Morris site had warmer temperatures, therefore increasing the rate of the soil's chemical processes compared to the soil landscape at Miniota. The Miniota site was more gradual in its elevation changes from the upper LEC to the lower LEC compared to Morris. The tillage disturbed and mixed the surface horizon in with the carbonate-rich, organically-poor subsoil material at Morris, but not at Miniota. This caused decreasing amounts of SOC and increasing amounts of carbonates to be exposed at the surface layer in the Morris landscape, which increased the soil pH.

In addition, the tillage action would not have easily allowed a stable organic carbon pool to form as the tillage was disrupting the soil's porosity and aggregate stability, and lessened surface residues, which are some of the factors that affect SOC formation. Many other studies have reported that tillage reduced SOC contents compared to zero-tilled sites (Mermut et al. 1983, Salinas-Garcia 1997, Elliot and Efetha 1999). As well, tillage may have an adverse impact on decreasing soil organic matter quality. Arshad et al. (1990) determined that the quality of soil organic matter was negatively impacted by 10 years of tillage in a British Columbia site. The tilled soil had lower amounts of carbohydrates and amino acids than the non-tilled site (Arshad et al. 1990).

The herbicide's average  $K_d$  value at Miniota (0.6 mL/g) was twice that of the average Morris  $K_d$  value (0.3 mL/g). A greater amount of 2,4-D was sorbed by soil in the Miniota site compared to the heavily-tilled site because the Miniota site contained more %SOC. This agrees with other pesticide sorption by soil studies where greater adsorption of alachlor (Locke 1992, Locke et al. 1996), atrazine (Novak 1999), sulfentrazone (Reddy and Locke 1998), cyanazine (Reddy et al. 1997a, Reddy et al. 1997b), and chlorimuron (Reddy et al. 1995) occurred on zero-tilled soils compared to their respective tilled soils, which was attributed to greater SOC in the zero-tilled soils. However, bentazon sorption was similar in both conventional and zero-tilled soils because of its very low sorption (Gatson et al. 1996).

The two study sites obtained the same average  $K_{OC}$  of 24.5 mL/g and had similar ranges of  $K_{OC}$  values from 8.3 mL/g to 57.2 mL/g. These equivalent  $K_{OC}$  values indicated that the mean amount of 2,4-D sorption per unit of organic carbon was similar and that the herbicide was not strongly bound to the soil constituents at both sites. Locke (1992) also determined that alachlor  $K_{OC}$  values from a conventionally tilled and from a zero-tilled site were not significantly different.

On average, the Miniota soils desorbed substantially more of the sorbed 2,4-D than the Morris soils. The average percent amount of sorbed herbicide that desorbed was 65.0 %  $\pm$  8.5% at Miniota compared to 48.7 %  $\pm$  11.1% for the Morris site. These results suggest that greater sorption at the Miniota site allowed for greater desorption, relative to Morris. A portion of the 2,4-D sorbed onto the Miniota soils was held by weaker bonding mechanisms relative to the 2,4-D sorbed onto the Morris soils. Reddy and Locke (1998) determined using Illinois soils that 71% of sorbed sulfentrazone desorbed from a conventionally tilled site versus 58% of sorbed sulfentrazone that desorbed from a zero-tilled site.

Regardless of the small differences in desorption, the soils at Miniota had more 2,4-D sorption and a reduced 2,4-D mobility compared to the Morris soils. The soils at Morris had a greater pH and a lower SOC content, thus less of the herbicide was sorbed compared to the Miniota site.

### **6.1.2 Spatial distributions of the soil properties and herbicide behaviour**

On average, the soil pH value of 7.56 of the Morris soils was greater than the soil pH value of 7.2 at Miniota. At Morris, the pH of the surface soil layer had become more alkaline due to the exposure of carbonates from the subsurface layer. The upper and middle LECs had more carbonates and more basic soil pH values relative to the lower LEC. At Miniota, the average soil surface pH value was 7.2 in which the average pH values increased from the upper LEC to the depressional LEC. The soil surface pH in this landscape was related with the hydrologic progression from well to imperfectly drained soils (Manning 1999). Perhaps since cultivation, the eluvial soils received bases from below via capillary action from a shallow water table (Manning 1999), thereby increasing the soil pH of the surface layer in the depressional LEC.

For both sites, SOC content increased from the upper to the middle to the lower LECs. This spatial distribution in the SOC content is due to landscape position differences in soil movement and in carbon mineralization. Both sites had the smallest average  $K_d$  values in the upper LEC samples, in which  $K_d$  increased downslope, to the middle and lower LECs. As such, in regions where more SOC existed, more of the herbicide was sorbed.

The distribution of the herbicide's  $K_{oc}$  did differ by LEC position for Morris, but not for Miniota. Again, this may be attributed to the differences in tillage management between the two fields. At Morris, the tillage disrupted the SOC and caused carbonates to be

exposed at the surface in the upper and middle LECs, which might have interfered with the 2,4-D sorption onto soil. This may have explained the lower  $K_{oc}$  value in the upper LEC at Morris.

At Miniota, the percentage of sorbed herbicide that desorbed did not differ within the LECs, whereas at Morris, herbicide desorption was greater in the upper LEC relative to the middle and lower LECs. This suggests that 2,4-D was less strongly sorbed in the upper slope positions of the Morris landscape. This variability may have been from the variability of the herbicide's  $K_d$  distribution since  $K_d$  and percent herbicide desorption were moderately correlated at Morris. As well, in the upper LEC, the herbicide was more in its anionic state (due to greater soil pH), which could indicate that the anionic form is released from the soil relatively easily.

### **6.1.3 Correlations between soil properties and the herbicide behaviour**

The herbicide's  $K_d$  did not have the same linear relation with %SOC for both sites. In the Miniota soils, the %SOC was more strongly correlated to  $K_d$  ( $r = 0.71$ ,  $P < 0.01$ ) than in the Morris soils ( $r = 0.23$ ,  $P < 0.01$ ). This large difference in the %SOC and  $K_d$  behaviour is likely due to the sites' differences in carbonate content, pH, and %SOC. In the Morris site, the large amounts of carbonates at the surface could have been interfering with the 2,4-D sorption process onto the SOC. This effect may have differed with landscape position as evident by the landscape differences in  $K_{oc}$  and in carbonate

contents. Modeling pesticide behaviour is also more difficult in eroded landscapes due to the narrow ranges of SOC values. When the  $K_d$  and SOC data from both sites were combined, a strong linear relation existed between these two variables ( $r = 0.82$ ,  $P < 0.01$ , Figure 6.1) as found by other researchers (Reddy and Gambrell 1987, Mallawatantri and Mulla 1992, Cheah et al. 1997, Farenhorst et al. 2001), i.e.  $K_d$  increased with increasing %SOC.

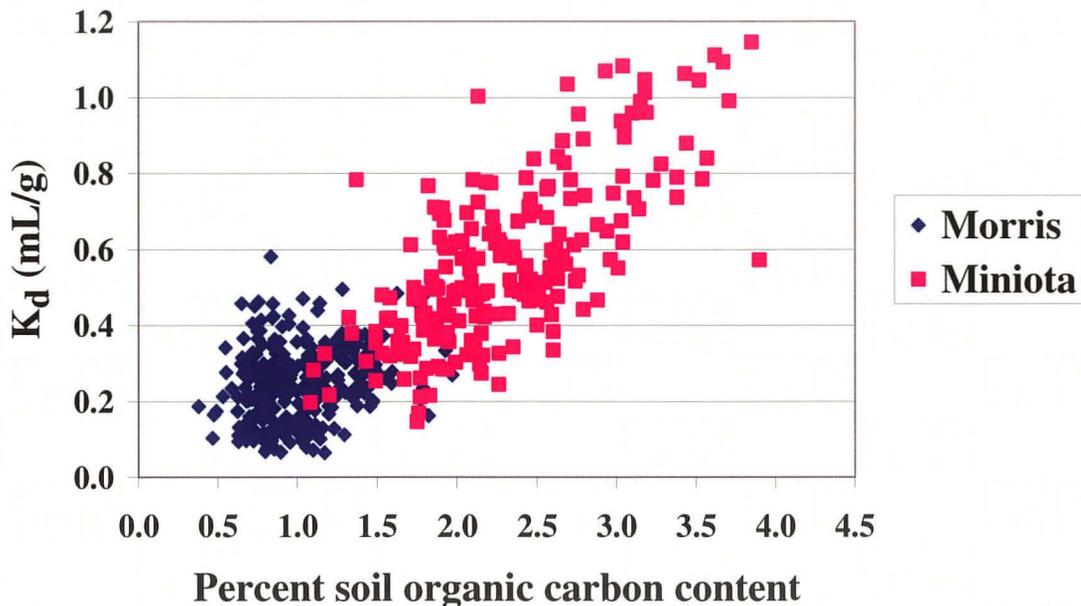


Figure 6.1 Correlation between % soil organic carbon content and the adsorption partition coefficient ( $K_d$ ) for 2,4-D for both study sites combined ( $K_d = 0.01 + 0.24\%SOC$ ,  $r = 0.82$ ,  $P < 0.01$ )

Predicting the sorption behaviour of 2,4-D within agricultural landscapes requires information on %SOC as this parameter is often the main determinant in the sorption of the herbicide onto soil. As well, soil pH measurements would be needed. For heavily-

tilled sites, modeling herbicide behaviour is more complex. Tillage erosion distributes significant amounts of soil from upper slope to lower slope positions, thereby altering the spatial variability of soil properties within the landscape. Results of this study also indicate that carbonates in eroded landscapes need to be measured for predicting  $K_d$ . As such,  $K_d$  prediction models would be different for heavily-tilled sites than for zero-tilled sites. More research is required to better comprehend how 2,4-D sorption is affected by soil carbonates and by other soil properties such as cation exchange capacity and iron oxides.

Soil surface pH's effect on the herbicide sorption and desorption was not the same for both sites. In Miniota, with its more acidic pH soils, the herbicide was more in its molecular form while at Morris, with its alkaline pH soils, the herbicide was more in its anionic form. In contrast to the Morris soil landscape, the herbicide's  $K_d$ ,  $K_{OC}$ , or percent desorption were not influenced by the soil pH at Miniota. When all of the soil pH values were correlated with all of the  $K_d$  values (i.e. data for both sites combined), the herbicide sorption decreased as pH increased (Figure 6.2). With each unit increase of soil pH, the amount of herbicide in anionic form increased tenfold. This again indicates that 2,4-D preferentially sorbs onto soil constituents when in molecular form, relative to being in the anionic form. In fact, the net negative charged soil constituents such as clay and humic substances may repel 2,4-D when in anionic form.

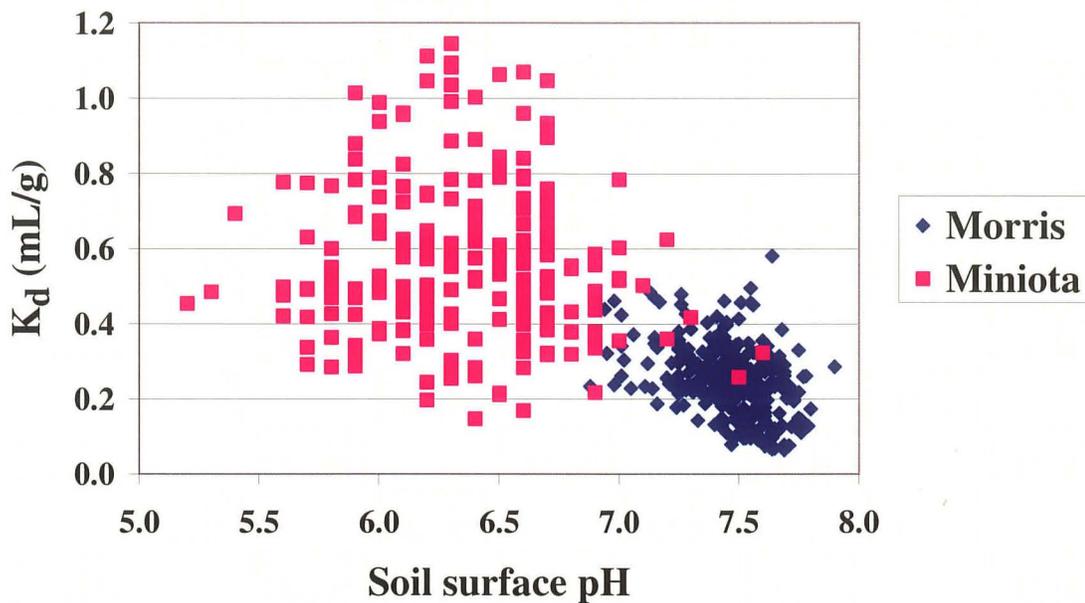


Figure 6.2 Correlation between the soil surface pH and the herbicide's  $K_d$  for both sites  
 $(K_d = 2.03 - 0.24\text{pH}, r = -0.68, P < 0.01)$

The correlation between  $K_{OC}$  and SOC differed for the two fields. For the Miniota site, no significant correlation existed between SOC and  $K_{OC}$ , whereas at Morris, the correlation was moderately negative with  $r = -0.42$  ( $P < 0.01$ ). For Morris, this indicated that the sorptive capacity of the organic carbon decreased with increasing organic carbon content. When both sites' data were plotted together, there appeared to be a very weak negative linear relation between SOC and  $K_{OC}$  (Figure 6.3).

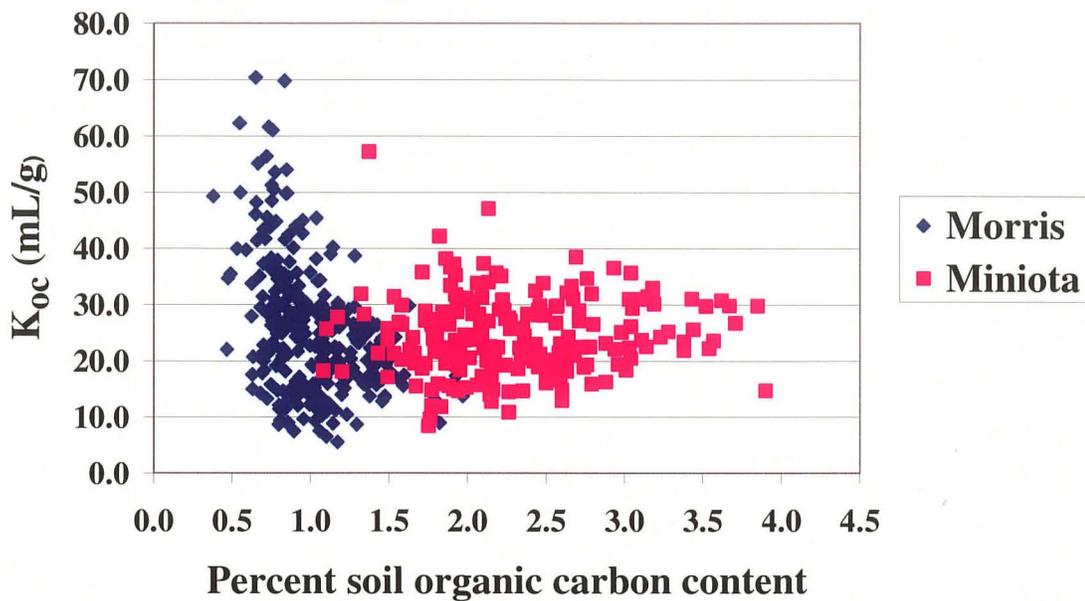


Figure 6.3 Correlation between  $K_{oc}$  and percent soil organic carbon content for 2,4-D for both study sites combined ( $K_{oc} = 27.63 - 1.70\%SOC$ ,  $r = -0.13$ ,  $P < 0.01$ ).

In both fields, the amount of herbicide desorption was negatively correlated with  $K_d$ . This indicates that as more of the herbicide was bound to the soil, less desorbed. For Miniota, %herbicide desorption was also correlated with %SOC ( $r = -0.23$ ,  $P < 0.01$ ). When the two sites' data were combined, two clusters of data resulted (Figure 6.4), which further indicated that the impact of SOC on herbicide desorption was site specific.

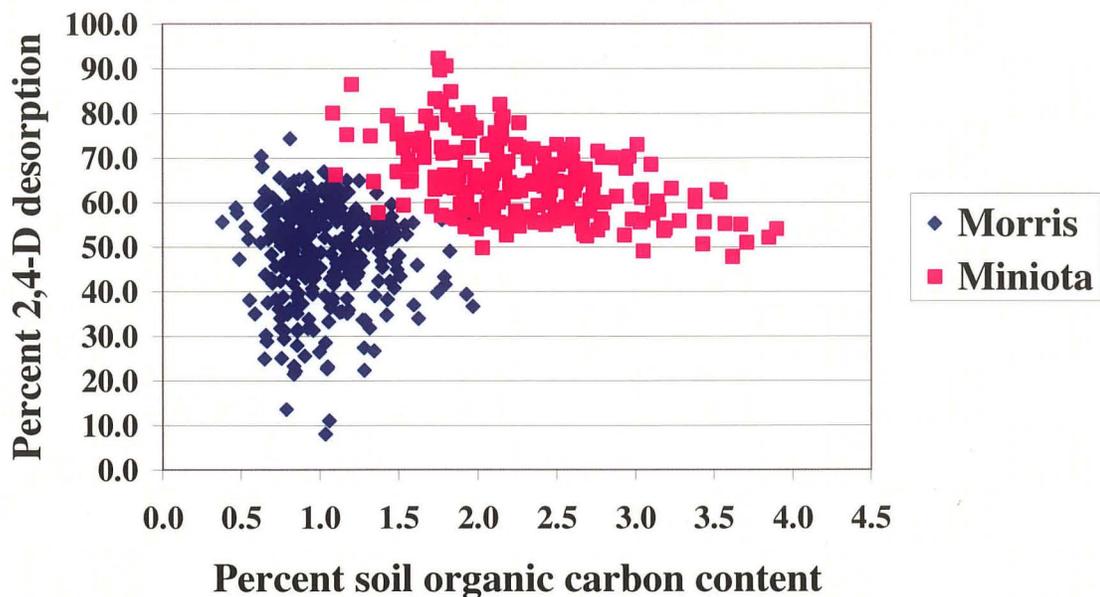


Figure 6.4 Correlation between percent soil organic carbon content and percent 2,4-D desorption for both sites combined. ( $\% \text{Desorption} = 44.67 + 6.90\% \text{SOC}$ ,  $r = 0.41$ ,  $P < 0.01$ )

## 6.2 Sources of error

All of the  $^{14}\text{C}$  2,4-D samples were analysed either in duplicates or in triplicates and all supernatants were sampled in duplicates. As the standard deviations of the  $K_d$  and percent herbicide desorption values were small, it is unlikely that analytical errors occurred. Examples of possible errors that may have occurred during the course of this herbicide study are:

1. The Beckman Liquid Scintillation Counter machine was utilized to analyse all  $^{14}\text{C}$  samples. This machine's counting efficiency may vary depending on factors such as the colour of the herbicide solution, scintillation cocktail mixtures, and the

concentration of the  $^{14}\text{C}$  2,4-D in the solutions. These may have affected its ability to properly analyse the samples.

2. The pH of the  $\text{CaCl}_2$  solutions may not have been always constant as new solutions were constantly made during the sorption and desorption experiments. A pH shift alters the net charge of ionizable pesticides and/or soil components, thus changing the sorption interactions directly (de Jonge and de Jonge 1999). Indirect effects are from a change in the degree of aggregation of the soil, which is strongly correlated to the soil solution composition (de Jonge and de Jonge 1999).

### **6.3 Recommendations for further studies**

For future studies involving pesticide sorption and desorption in landscapes, a few recommendations are suggested here:

1. If studying more than one site the soil sampling methodology should be kept constant at all sites. Identifying the soil series that are present in these sites, will aid in understanding the sites' soil formation processes and in the spatial variability of pesticide sorption.
2. For all soil samples, percent soil organic carbon and soil pH should be measured, as these properties will influence the sorption of the herbicide. Other soil properties to measure may include the site's clay content, mineralogy, and cation exchange capacity.

3. Should the site be in a heavily-tilled carbonate-rich, eroded landscape, the carbonates should be measured as well from all collected soil samples. In addition, if possible, soil samples should be collected from a nearby untilled site of similar soils to help determine the impacts of tillage on the soil properties.
4. While both  $K_d$  and  $K_{oc}$  are important input parameters in pesticide research, screening (Wagenet and Rao 1985), and fugacity models (Wauchope et al. 2002), the spatial variations in 2,4-D  $K_d$  and  $K_{oc}$  values from the literature and from this study, point the need for using caution when modeling pesticide mobility in soil (Locke 1992) while using these coefficients.
5. In addition, pesticide desorption is one of the many processes that controls pesticide movement in the environment. However, little is known about the spatial variability of pesticide desorption within agricultural landscapes. Therefore, understanding pesticide's ability to desorb is another factor that needs to be considered when modeling pesticide behaviour in the environment.

## 7. SUMMARY AND CONCLUSIONS

This study examined the spatial variability of soil properties and 2,4-Dichlorophenoxy acetic acid (2,4-D) sorption and desorption in two prairie calcareous landscapes. The first site was in a heavily tilled field situated near Morris, MN., which was characterized by the presence of subsoil carbonates at the soil surface in the upper shoulder landscape positions. The second study site was a gently undulating glacial till landscape situated near Miniota, MB. In order to describe the spatial variability of the two sites, both sites were delineated into landform element complexes (LECs) by the use of a landform description model. These two sites were split into upper, middle, lower, and depressional LECs.

In the first set of experiments, concerns existed about soil microbiological processes (i.e. the degradation of the 2,4-D by soil microorganisms during the batch equilibrium experiments) interfering with the sorption of the 2,4-D onto soil. As such, mercuric chloride was used as a soil sterilizer and was found to not be a suitable choice using the Miniota soils. The mercuric chloride decreased the capacity of the soil to retain the 2,4-D and the interference of the mercuric chloride with herbicide sorption increased with increasing amounts of soil organic carbon.

In the landscape studies, various soil properties and 2,4-D sorption and desorption varied with landscape position as a result of various soil formation processes and land

management at the two sites. In both sites, %SOC contents increased from the upper to the lower LECs. The herbicide was weakly bound to the soil constituents in both sites, however, on average, the herbicide sorption by soil at Miniota (0.6 mL/g) was twice the amount of herbicide sorption at Morris (0.3 mL/g). The herbicide's  $K_d$  did differ with LEC where the lower and depressional LECs sorbed the most 2,4-D relative to the upper and middle LECs.

In the Miniota site, percent soil organic carbon content was the main determinant in the sorption of 2,4-D onto soil ( $r = 0.71$ ,  $P < 0.01$ ), which is in agreement with many other 2,4-D sorption studies. In the eroded Morris landscape, (which is typical for tilled hummocky terrains in Canada and the United States), the 2,4-D sorption was not well correlated with %SOC ( $r = 0.23$ ,  $P < 0.01$ ), because the landscape was characterized by small amounts of %SOC, elevated amount of carbonates, and alkaline pH conditions. For Morris, the intensive tillage action had increased the amounts of carbonates at the soil surface, which then increased surface soil pH. This basic soil pH caused a greater portion of the herbicide to be more anionic, which was repelled by the soil's negative charge therefore also contributing to the herbicide's weak sorption. The exposed carbonates could also have interfered with the sorption of the herbicide onto the soil organic carbon, which made predicting  $K_d$  by %SOC difficult.

Even though the same average  $K_{oc}$  value was obtained for both sites, (24.5 mL/g) the  $K_{oc}$  did not differ with LEC at Miniota, while at Morris the  $K_{oc}$  did differ with LEC. The

tillage action at Morris disrupted the site's soil organic carbon quality and quantity and caused carbonates to be exposed at the surface in the upper and middle LECs. With carbonates present in large quantities (i.e. > 10.0%) in some of the soil samples in the upper LEC, they could have been interfering with the herbicide sorption onto the soil organic carbon, thus leading to a reduced  $K_{oc}$  value.

More of the sorbed herbicide desorbed back into the soil solutions at Miniota (65.0%) than at Morris (48.7%). At Morris, the amount of herbicide desorption differed amongst the LECs, but not at Miniota. The upper LEC significantly desorbed more of the herbicide at Morris relative to the middle and lower LECs. This variability may have been from the variability of the herbicide's  $K_d$  distribution since  $K_d$  and %herbicide desorption were moderately correlated across the Morris site. As well, in the upper LEC, the herbicide was more in its anionic state, which could indicate that the anionic form of the herbicide is released from the soil more easily, relative to the other LECs.

Additional research is required to fully more comprehend the effects that carbonates have on the sorption and desorption of the 2,4-D. As well, other soil properties (i.e. cation exchange capacity and iron oxides) that were not measured should be examined if they affect herbicide behaviour within prairie calcareous landscapes.

## 8. CONTRIBUTION TO KNOWLEDGE

This is the first study that used the LEC classification system in modeling the spatial distribution of herbicide sorption and desorption in landscapes. The results of this study show that soil organic carbon has a poor relation to herbicide sorption in heavily-tilled landscapes. This has not been observed in other pesticide sorption studies. This study suggested that soil carbonates influenced the amount of 2,4-D sorbed by soil. This also has not been reported in the literature and requires further research. This information is important, as large areas of hummocky tilled agricultural land exist in the United States and in Canada, which undergo heavy pesticide application. These areas with lower SOC contents and exposed subsoil carbonates would then be more susceptible to pesticide contamination of groundwater and surface waters.

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## 10. APPENDICIES

Appendix IA. Detailed descriptions of the soil series found within the Morris study area as classified by Diedrick (1972) unless otherwise noted.

### **The Barnes series:**

This series is characterized as fine-loamy, mixed, frigid Calcic Hapludolls (United States Department of Agriculture and National Resources Conservation Service 1999a). “It consists of deep, well drained soils that have developed in calcareous loam glacial till. In a representative profile, the surface layer is neutral, black loam about 20 cm thick. The subsoil is neutral loam about 28 cm thick. The upper part is very dark grayish brown, and the lower part is dark grayish brown. The underlying material is a calcareous, light olive-brown loam.

The organic-matter content, available water capacity, and natural fertility are high. Erosion control and fertility management are the major concerns in using these soils.”

The mollic epipedon is 18 to 40 cm thick (United States Department of Agriculture and National Resources Conservation Service 1999a). The 22 to 100 cm particle-size control section is loam or clay loam and contains up to 10 percent by volume of rock fragments (United States Department of Agriculture and National Resources Conservation Service 1999a). It has more than 30 percent total sand and more than 20 percent fine sand and coarser sand. Stony phases are recognized (United States Department of Agriculture and National Resources Conservation Service 1999a).

### **The Buse series:**

This series is characterized as fine-loamy, mixed, frigid Typic Calciudolls. It consists of very deep, well drained soils that formed in loamy glacial till on moraines (United States Department of Agriculture and National Resources Conservation Service 1998). These soils have moderate and moderately slow permeability (United States Department of Agriculture and National Resources Conservation Service 1998). They have slopes of 3 to 50 percent (United States Department of Agriculture and National Resources Conservation Service 1998).

The mollic epipedon ranges from 18 to 25 cm in thickness (United States Department of Agriculture and National Resources Conservation Service 1998). Free carbonates typically are at the surface or are in all parts of the upper 18 cm when mixed (United States Department of Agriculture and National Resources Conservation Service 1998). The rock fragment content ranges from 2 to 10 percent throughout (United States

Department of Agriculture and National Resources Conservation Service 1998). The 25 to 100 cm control section averages between 18 and 30 percent clay and between 15 and 40 percent of fine sand and coarser particles (United States Department of Agriculture and National Resources Conservation Service 1998).

#### **The Darnen series:**

This series is characterized as fine-loamy, mixed, superactive, frigid Cumulic Hapludolls (United States Department of Agriculture and National Resources Conservation Service 2000b). “This series consists of deep, moderately well drained soils that have developed in material washed down from the nearby glacial till soils. These soils are nearly level to gently sloping; they lie in drainageways or at the base of slopes.”

In a representative profile, the surface layer is neutral, very dark grayish-brown silt loam about 50cm thick. The subsoil is neutral, very dark grayish-brown loam about 33 cm thick. The underlying material is light olive-brown loam that is neutral in the upper few inches and calcareous in the lower part.

The organic-matter content, available water capacity, and natural fertility are high. Permeability is moderate.”

The mollic epipedon ranges from 60 to 120 cm in thickness. Depth to free carbonates is 50 to 152 cm (United States Department of Agriculture and National Resources Conservation Service 2000b). The control section has 18 to 30 percent clay and from 15 to about 35 percent fine sand and coarser. Pedons have fine strata from downslope soil movement (United States Department of Agriculture and National Resources Conservation Service 2000b). Pedons commonly are free of rock fragments, but some have as much as 5 percent of the volume, mostly below 30 inches (United States Department of Agriculture and National Resources Conservation Service 2000b).

#### **The Estelline series:**

The Estelline series are fine-silty over sandy or sandy-skeletal, mixed, superactive, frigid Calcic Hapludolls (United States Department of Agriculture and National Resources Conservation Service 2001). They consist of very deep, well drained soils formed in silty material overlying sand and gravel on stream terraces and glacial outwash plains. Permeability is moderate in the upper mantle and very rapid in the sand and gravel (United States Department of Agriculture and National Resources Conservation Service 2001). Slopes range from 0 to 9 percent (United States Department of Agriculture and National Resources Conservation Service 2001).

The thickness of the mollic epipedon ranges from 7 to 16 inches and extends into the Bw horizon (United States Department of Agriculture and National Resources Conservation

Service 2001). The control section typically is silt loam or silty clay loam averaging between 18 and 30 percent clay (United States Department of Agriculture and National Resources Conservation Service 2001). Depth to sand and gravel commonly is about 36 inches, but ranges from 22 to 40 inches (United States Department of Agriculture and National Resources Conservation Service 2001). Depth to free calcium carbonate ranges from 15 to 40 inches (United States Department of Agriculture and National Resources Conservation Service 2001).

Estelline soils are on stream terraces or glacial outwash plains (United States Department of Agriculture and National Resources Conservation Service 2001). Slopes are plane to convex and gradients are usually less than 3 percent but range from 0 to 9 percent (United States Department of Agriculture and National Resources Conservation Service 2001). These soils formed in a silty material overlying sand and gravel glacial outwash (United States Department of Agriculture and National Resources Conservation Service 2001).

### **The Langhei series:**

This series is characterized as a fine-loamy, mixed, superactive, frigid Typic Eutrudepts (United States Department of Agriculture and National Resources Conservation Service 2000c). “This series consist of deep, somewhat excessively drained soils that have developed in calcareous loam till. These are undulating to very steep soils.

In a representative profile, the surface layer is calcareous very dark grayish-brown loam about 20 cm thick. The underlying material is light olive-brown loam. The upper 30 cm is strongly calcareous. Below this to a depth of 152 cm, the material is calcareous.

Organic matter content is low, available water capacity is high, and permeability is moderate. Natural fertility is low because of the high lime content. Erosion, low fertility and droughtiness are the major limitations to use of these soils.”

The particle size control section typically averages between 18 and 25 percent clay, with an extreme range 18 to 30 percent (United States Department of Agriculture and National Resources Conservation Service 2000c). It averages 15 to 40 percent fine sand and coarser (United States Department of Agriculture and National Resources Conservation Service 2000c). It typically has about 2 to 10 percent by volume of rock fragments of mixed lithology (United States Department of Agriculture and National Resources Conservation Service 2000c).

### **The Parnell series:**

The Parnell series are fine, smectitic, frigid Vertic Argiaquolls (United States Department of Agriculture and National Resources Conservation Service 2003). They are very deep, very poorly drained and poorly drained soils that formed in water-sorted sediments from glacial drift in depressions, swales and drainageways on glacial moraines (United States

Department of Agriculture and National Resources Conservation Service 2003). These soils have slow permeability. Slopes range from 0 to 3 percent (United States Department of Agriculture and National Resources Conservation Service 2003).

A typical Parnell pedon is a silty clay loam with a nearly level slightly concave slope located in a depression in a glacial moraine (United States Department of Agriculture and National Resources Conservation Service 2003). Depth to free calcium carbonate ranges from 89 to over 203 cm (United States Department of Agriculture and National Resources Conservation Service 2003). Pedons typically do not have rock fragments, but some pedons contain as much as 8 percent, by volume, in the lower part of the B horizon and in the C horizon (United States Department of Agriculture and National Resources Conservation Service 2003). Stony surface phases have been recognized (United States Department of Agriculture and National Resources Conservation Service 2003). Some pedons have an 0a horizon as much as 15 cm thick (United States Department of Agriculture and National Resources Conservation Service 2003). The mollic epipedon ranges from 61 to 203 cm in thickness and typically includes all or part of the B horizon (United States Department of Agriculture and National Resources Conservation Service 2003).

The Parnell soils formed mostly in water-sorted sediments from glacial till (United States Department of Agriculture and National Resources Conservation Service 2003). Calcareous loam or clay loam glacial till commonly underlies these sediments (United States Department of Agriculture and National Resources Conservation Service 2003).

### **The Svea series:**

This series is characterized as fine-loamy, mixed, superactive, frigid Pachic Hapludolls (United States Department of Agriculture and National Resources Conservation Service 1999b). “This series consists of deep moderately well drained soils that have developed in calcareous loam glacial till. They are nearly level to gently sloping soils.

In a representative profile, the surface layer is neutral, black loam, about 33cm thick. The subsoil is neutral, very dark grayish-brown to dark grayish-brown loam about 23 cm thick. The upper part of the underlying material is a calcareous to strongly calcareous, mottled, grayish-brown loam. The loamy part is calcareous, light olive-brown loam.

The organic matter content, available water capacity, and natural fertility are high. Permeability is moderate. They respond well to management.”

The 22 to 102 cm control section averages between 18 and 28 percent clay and 14 to 45 percent fine sand or coarser (United States Department of Agriculture and National Resources Conservation Service 1999b). It typically contains 1 to 10 percent by volume of rock fragments throughout (United States Department of Agriculture and National Resources Conservation Service 1999b). The mollic epipedon ranges from 41 to more

than 76 cm in thickness and may include part or the entire Bw horizon (United States Department of Agriculture and National Resources Conservation Service 1999b). Stony phases are recognized (United States Department of Agriculture and National Resources Conservation Service 1999b).

Appendix IB. Detailed descriptions of the soil series found within the Miniota study site, as classified by Fitzmaurice et al. (1999).

### **The Angusville series:**

“This series is characterized by a Gleyed Eluviated Black Chernozemic soil profile formed on moderately to strongly calcareous, somewhat stony, fine loamy (L-CL) morainal till of limestone, granitic, and shale bedrock source. These soils are imperfectly drained and are located in lower to middle slope positions of undulating to hummocky landscapes, in close association with the well drained Newdale, Rufford, and Cordova soils, the imperfectly drained Varcoe series, and the poorly drained Drokan and Penrith series. Surface runoff is slow to moderately slow; permeability is moderately slow to slow within the solum and is moderately slow in the subsoil.

The average thickness of the soil profile is 61 cm and varies from 45 to 85 cm. The A horizon has a mean thickness of 25 cm and ranges from 20 to 40 cm. The very dark to gray Ap horizon is 15 to 20 cm thick, and the dark gray to gray Ae (Ahe) horizon, 5 to 15 cm thick. The dark brown to dark yellowish brown Btgj is 25 to 25 cm thick. A lime enriched later of 10 to 20 cm may be present. The C horizon is light olive brown with yellowish brown mottles.

The soils in this series have profiles that are thicker and more strongly developed and free of lime carbonates in comparison to the closely associated, shallower, carbonate-rich Gleyed Rego Black Varcoe series. The strongly leached Angusville are sites of net surface water infiltration and are thought to be sites of local recharge to the groundwater table.”

### **The Newdale series:**

“This series is characterized by an Orthic Black Chernozemic solum developed on moderately to strongly calcareous, loamy (CL) morainal till of limestone, granitic rock and shale origin. These soils are well drained and occur in middle to upper slope positions of undulating to hummocky landscapes. Surface runoff is moderate to moderately rapid; permeability is moderately slow.

The Newdale solum has a black to very dark gray Ah horizon, commonly 20 cm thick and ranging from 15 to 40 cm, a dark brown Bm horizon, 10 to 30 cm thick and a transitional BC horizon, 3 to 15 cm thick. A lime carbonate horizon, 10 to 15 cm thick

may be present in shallower soils but is not evident in deeper profiles. Its solum depth averages 40 cm and ranges from 25 to 60 cm. Minor amounts of well drained Eluviated Black soils occur within the Newdale mapping units. These eluviated soils range from 75 cm to greater than 1 m in depth. They have thick A (combined Ah, Ahe) horizons, 30 to 60 cm and Bt horizons that are 40 cm thick.

The Newdale series in the study area differ from the very similar Rufford and Cordova soils in being more strongly leached, thicker, and free of lime carbonate in the A and B horizons.”

**The Varcoe series:**

“This series is characterized by a Gleyed Rego Black (carbonate-rich) Chernozemic solum on moderately to strongly calcareous, loamy (L, CL) morainal till of limestone, granitic rock and shale origin. These soils are imperfectly drained and occur in the lower slope positions of undulating to hummocky landscapes in close association with Angusville series. They receive runoff from the upper slopes, and in some landscapes, may be influenced by seepage from adjacent lower lying areas. Permeability is slow and may be restricted during periods of subsoil saturation. In areas where seepage waters contain soluble salts, there may be a risk of soil salinization.

Varcoe profiles average 42 cm in thickness and range from 20 to 60 cm. The A horizon is usually 25 cm thick and ranges from 20 to 50cm; very dark in color and is underlain by a dark gray transitional AC horizon, 4 to 8 cm thick. A lime accumulation horizon may be present, but is often thin and discontinuous.”