

## **SORPTION OF HERBICIDES IN RELATION TO SOIL VARIABILITY AND LANDSCAPE POSITION**

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### **ABSTRACT**

Using the soil-water sorption partitioning coefficient ( $K_d$ ), this study quantified the spatial variation of 2,4-D sorption by soil in an undulating-to-hummocky terrain landscape near Minnedosa, MB, Canada. Herbicide sorption was most strongly related to soil organic matter content and slope position, with greatest sorption occurring in lower landscape positions with greater soil organic matter content. The relation between sorption and slope position was more pronounced under conventional tillage (CT) than under long-term zero-tillage (ZT). Using multivariate regression and three independent variables (soil organic matter content, soil clay content and soil pH), the prediction of herbicide sorption by soil was very good for CT ( $R^2 = 0.89$ ) and adequately for ZT ( $R^2 = 0.53$ ).

*Key Words:* Herbicide; Sorption; Partitioning coefficient; Landscape position; Zero-tillage; Conventional-tillage.

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## INTRODUCTION

Herbicides are an important strategy in North American agriculture, particularly with the increasing use of reduced-tillage systems. Herbicides are generally applied over very large areas of agricultural land and the potential for surface-water and groundwater off-site pollution is a concern (1). Understanding the underlying factors and mechanisms determining the fate of herbicides in agricultural systems is important to minimize nonpoint-source contamination and to improve the quality of water used for drinking, irrigation and recreational purposes. Studying herbicide fate in agricultural landscapes is also important for defining effective weed control decisions.

The fate of herbicides in soils is controlled by transformation, retention and transport processes. A variety of research, screening and management models have been proposed to describe and simplify herbicide reactions in soils (2). The most sensitive input parameter in many of these herbicide fate and transport models is the soil-water sorption partitioning coefficient, a measure of herbicide sorption by soil. Herbicide sorption in soil has been shown to influence herbicide volatilization, degradation and leaching rates, and herbicide uptake by plants and soil fauna (3,4,5). Complete understanding of herbicide sorption processes in soils is essential to a more fundamental comprehension of the fate of herbicides in soils, and to further advance models for improving pesticide fate prediction in the field.

Pesticide sorption by soil is influenced by the molecular characteristics of the pesticide, and the physical, chemical and biological properties of the soil. For example, sorption of a given pesticide varies with soil clay content and mineralogy (6), soil organic matter content and composition (7), soil pH, temperature and moisture content (8), soil microbial biomass (9), and earthworm biomass in soil (10,11).

Studies have found that spatial variation of selected soil properties within fields reflected differences in landscape position and explained much of the measured variation in herbicide sorption within fields for the herbicides atrazine (12), imazethapyr (13), and metolachlor (14). For most herbicides, the soil organic carbon content was the most important factor controlling herbicide sorption by soil (12). To date, there are few reports that quantify how the spatial distribution of herbicide sorption within the landscape is influenced by land management practices (15).

The herbicide 2,4-D [(2,4-(dichlorophenoxy)acetic acid] is widely used in North America for the post-emergent control of broadleaf weeds in a variety of crops. It is also a frequently detected herbicide in river waters (16). The objective of this study was to quantify and correlate the spatial variability of soil properties and 2,4-D sorption at the field-scale in a conventional- and zero-tilled field.



## MATERIAL AND METHODS

### Site Description

The study site selected was located 3 km northwest of Minnedosa, MB, Canada, and consisted of two adjacent zero- (ZT) and conventional (CT) tilled fields. The ZT field was last cultivated in 1977, 21 years prior to the collection of the soil samples. While agronomic practices other than tillage were not necessarily identical for both fields, the differences in tillage practices over the 21 years was the major management contrast between the two fields. The landscape of the study site was an undulating-to-hummocky terrain with five soil series (Angusville, Beresford, Cordova, Newdale and Varcoe series) developed on glacial till of mixed limestone, shale and granite origin. The dominant texture of the surface soil (Ap-horizon) was clay loam.

### Soil Sampling and Analysis

Both fields were georeferenced (global positioning system). Soil samples were collected along four parallel transects 1000 m long, each 50 m apart, spanning both fields. Sampling points along transects were spaced at intervals of 50 m. Soil samples were collected for all soil horizons but the study reported here only used samples that were taken from 0 to 15 cm depth in the conventional-tilled field and from 0 to 8 cm in the zero-till field. Because of tillage, we assumed that the soil characteristics of the Ap horizon in the CT field were uniform throughout the 15-cm depth. Hence soil characteristics, measured for the entire Ap horizon, represented the surface layer (0–8 cm) as well. In total, 80 surface soil samples were subjected to 2,4-D sorption analysis. For these samples, total carbon was measured by dry combustion in a Leco furnace model CHN-600, and inorganic carbon was determined by measuring carbon dioxide evolved after digestion with 6M HCL. Soil pH was measured in CaCl<sub>2</sub> using a 1 : 1 ratio. Soil texture was measured using the hydrometer method (17).

### Chemicals and Analytical Methods

[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) was used in experiments to determine the sorption of 2,4-D by soil. Herbicide stock solutions for experiments were prepared in 0.01 M CaCl<sub>2</sub> by mixing the [U-ring-<sup>14</sup>C]2,4-D with analytical-grade 2,4-D (95% purity, Sigma Chemical Co., St. Louis, MO). The amount of radioactivity in herbicide solutions and samples from experiments was determined by Liquid Scintillation Counting (LSC) (LS 7500 Beckman Instruments, Fullerton, CA) using 10 ml of Scintisafe scintillation cocktail (Fairlawn, NJ).



### Partitioning Coefficients

Batch equilibrium measurements were conducted in triplicates to quantify the sorption of 2,4-D by soil. Experimental procedures were as follows: The herbicide stock solution was prepared to give a radioactive concentration of  $17 \text{ Bq L}^{-1}$  and a total 2,4-D concentration of  $10 \text{ mg L}^{-1}$ . The herbicide solution (10 mL) was added to 5 g of air-dry soil in 50 ml Teflon centrifuge tubes and placed in a rotary shaker for 24 hrs at room temperature in the dark to reach equilibrium. Previous batch experiments have shown that 2,4-D sorption on soil occurs rapidly, with most of the herbicides being removed from solution within the first few hours, and that a 24 h equilibrium period is sufficient to characterize the second phase of slow sorption (15). Preliminary testing revealed that 2,4-D did not adsorb onto Teflon. The soil slurries were then 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 LSC. Amount of herbicide adsorbed on soil was determined by the difference between the initial and equilibrium herbicide concentration. The sorption distribution coefficient,  $K_d \text{ [L/Kg]}$ , was calculated assuming linear partitioning ( $1/n = 1$ ):  $K_d = (X/M) / C_e$ , where  $X/M$  = amount of herbicide adsorbed  $[\text{g}]$  / amount of adsorbent  $[\text{1/Kg}]$  and  $C_e$  = herbicide concentration of equilibrium solution  $[\text{g/L}]$ .

Statistical analysis included correlation using Statgraphics Plus 3.0 software (Statistical Graphics Corp.) and multiple linear regression using SigmaStat 2.03 (SPSS inc.).

## RESULTS AND DISCUSSION

Soil organic matter content ranged from 1.78 to 4.46% for ZT, and from 0.78 to 4.68% for CT. Soil organic matter content was on average greater for ZT ( $3.13\% \pm 0.60$ ) than for CT ( $2.31\% \pm 0.86$ ). Zero-till soils contain often larger amounts of organic matter than conventional-tilled soils (18).

Variability of soil pH within the landscape was small for both fields. Soil pH ranged from 6.0 to 8.0 and from 6.6 to 8.1, with average values of  $7.2 \pm 0.5$  and  $7.4 \pm 0.4$ , for ZT and CT, respectively. Clay content was more variable in ZT ( $20.85\% \pm 8.30$ ) than CT ( $18.42\% \pm 4.61$ ), and ranged from 12 to 46% (ZT) and from 8 to 31% (CT).

The herbicide 2,4-D was weakly sorbed by soil, as might be expected. The sorption distribution coefficient ranged from 0.12 to 1.33 L/Kg for ZT, and from 0.11 to 0.97 L/Kg for CT. The amount of herbicide sorbed by soil was on average slightly greater for ZT ( $0.56 \text{ L/Kg} \pm 0.25$ ) than for CT ( $0.51 \text{ L/Kg} \pm 0.19$ ). The  $K_d$  values obtained in this study resemble the values obtained by other studies for soils with a similar organic matter content (15).

Herbicide sorption in the CT field was only significantly correlated with soil organic matter content (Table 1). For ZT, herbicide sorption by soil was correlated



**Table 1.** Pairwise Coefficients of Linear Correlation of the Soil-Water Sorption Partitioning Coefficient ( $K_d$ ) with Soil Properties (Significance Levels Are in Brackets)

	Soil Organic Carbon	Soil pH	Soil Clay Content
$K_d$ – zero-till field	0.63 (0.00)	0.10 (0.62)	0.61 (0.00)
$K_d$ – conventional-tilled field	0.89 (0.00)	–0.21 (0.20)	–0.04 (0.79)

**Table 2.** Regression Equations Describing Dependency of the Soil-Water Sorption Partitioning Coefficient ( $K_d$ ) on Soil Organic Carbon Content (OC), pH, and Clay Content

Regression Equation	$R^2$
<b>Zero-till field</b>	
$0.754 + 0.228OC - 0.159pH + 0.0118clay$	0.530
$-0.203 + 0.174OC + 0.0111clay$	0.469
$0.736 + 0.314OC - 0.160pH$	0.422
$0.640 - 0.0712pH + 0.0211clay$	0.385
$0.160 + 0.0196clay$	0.370
$-0.220 + 0.249OC$	0.351
$0.295 + 0.0366pH$	0.005
<b>Conventional-tilled field</b>	
$0.152 + 0.199OC - 0.00541clay$	0.899
$0.466 + 0.193OC - 0.0544pH$	0.896
$0.639 + 0.196OC - 0.0635pH - 0.00606clay$	0.889
$0.0586 + 0.196OC$	0.823
$1.372 - 0.109pH - 0.00299clay$	0.221
$1.281 - 0.104pH$	0.209
$0.544 - 0.00178clay$	0.043

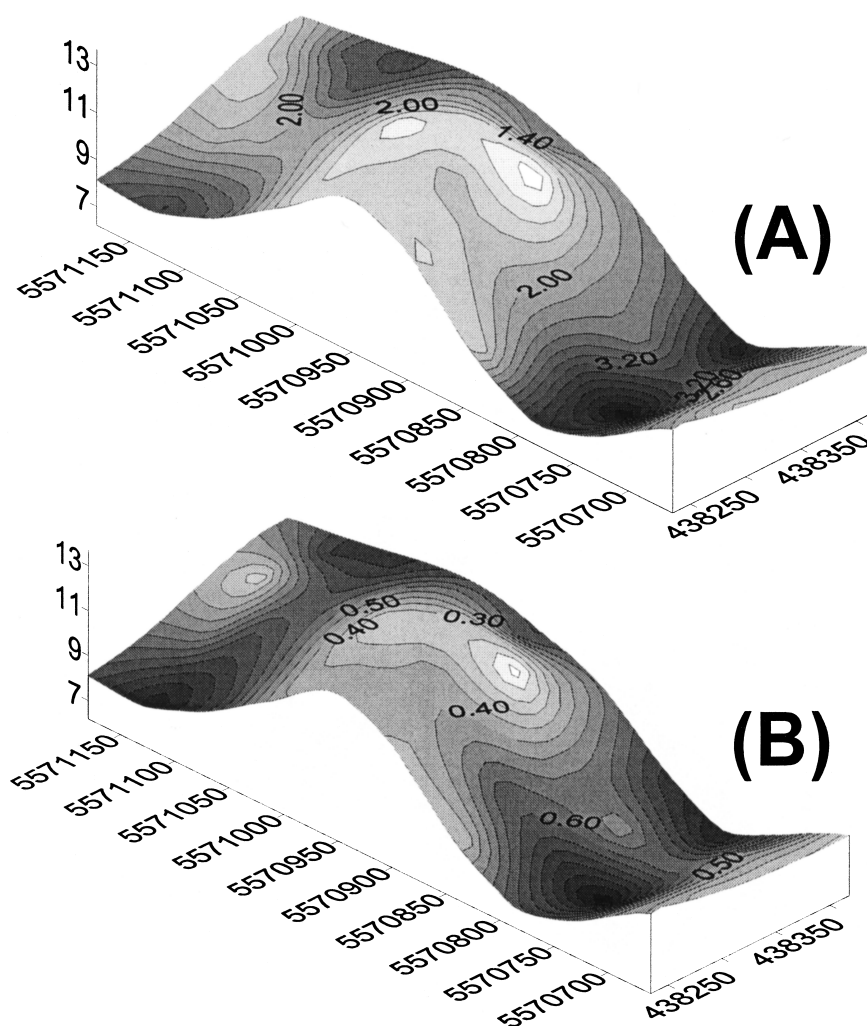
significantly with both soil organic carbon content and clay content. Other studies have shown that soil organic matter is an important factor in the sorption of 2,4-D by soil and sediment (19,20). It is likely that there was a range of adsorption mechanisms and sorption intensities responsible for the retention of 2,4-D by soil such as hydrogen-bonding van der Waals forces and hydrophobic partitioning (21,22,23).

Multiple linear regression for ZT revealed that the best prediction was made by using soil organic carbon in combination with clay content and/or soil pH, but the prediction was average ( $R^2=0.53$ , Table 2). For CT, the prediction of  $K_d$  was very good ( $R^2=0.82$ ) with soil organic carbon as the sole independent variable. Including clay content and/or did not improve the prediction to a great extent (Table 2).

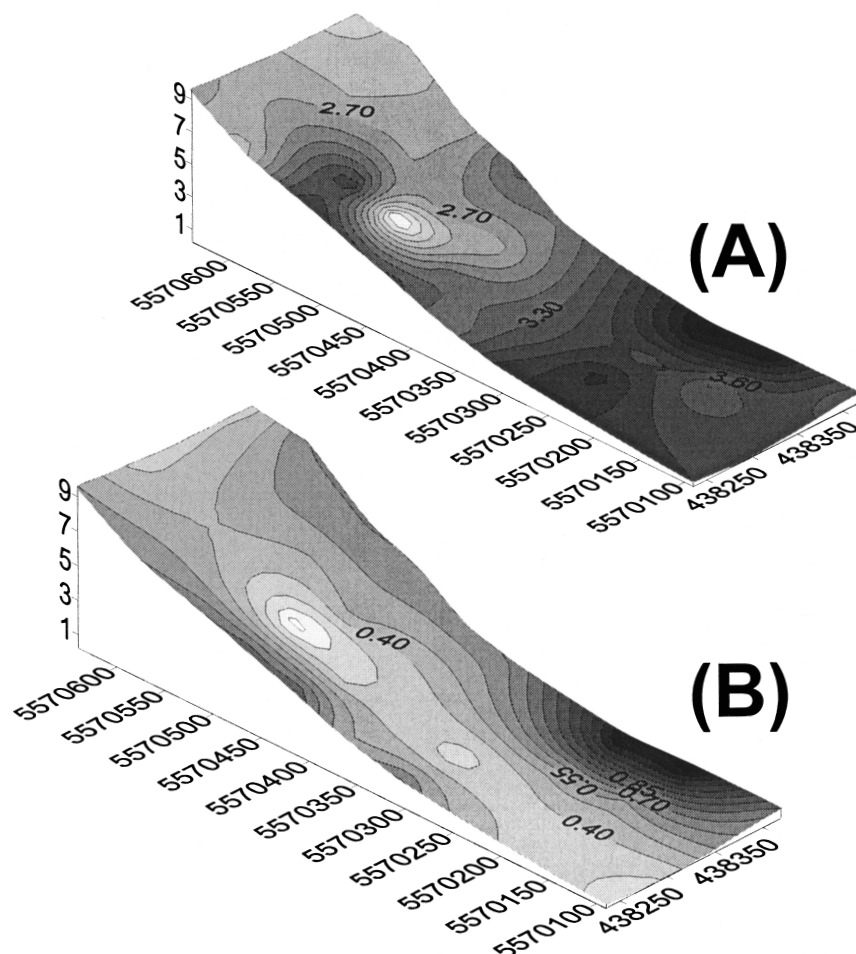


The spatial dependency between soil organic matter content and herbicide sorption by soil was very evident in CT (Fig. 1), but was present to a lesser extent in ZT (Fig. 2). The results for CT were better than for ZT, most likely, because the range of soil organic matter content within the landscape was larger for CT than for ZT. This was expected as water, wind and tillage erosion rates are usually larger for conventional-tilled fields, relative to conservation-tilled sites (24). With a larger range of soil organic matter content in the landscape, spatial differences in herbicide sorption by soil are also larger.

Soil organic carbon content was greater at bottom-slope position and caused



**Figure 1.** The spatial distribution of soil organic carbon content [%] (A) and the 2,4-D soil-water sorption partitioning coefficient [L/Kg] (B) in the conventional-tilled field.



**Figure 2.** The spatial distribution of soil organic carbon content [%] (A) and the 2,4-D soil-water sorption partitioning coefficient [L/Kg] (B) in the zero-till field.

increased adsorption of 2,4-D by soil, relative to the top-slope positions (Fig. 1 and 2). Because soil organic content was strongly related to slope position, the extent of herbicide sorption by soil can also be estimated based on landscape position. Slope position and soil properties such as soil organic carbon are more readily determined than herbicide sorption partitioning coefficients and therefore may serve as easier input parameters in screening and management models for predicting herbicide behavior in soil.

## CONCLUSION

Soil organic matter content, soil clay content, soil pH, and the 2,4-D soil-water partitioning coefficient was measured for 80 grid-points in an undulating-to-





hummocky terrain landscape near Minnedosa, MB, Canada. Using multivariate regression and the three soil characteristics as independent variables, the prediction of herbicide sorption by soil was very good for a conventional-tilled field ( $R^2 = 0.89$ ) and adequately for a zero-till field ( $R^2 = 0.53$ ). Soil organic carbon content was the most important soil characteristic influencing the soil-water partitioning coefficient. Upper-slope positions with lesser soil organic carbon content showed lesser herbicide retention by soil, relative to lower-slope positions with greater soil organic matter content. Since sorption is one of the most important processes influencing herbicide fate and movement in soil, our results have practical implications for the development of management strategies (e.g. site-specific and variable-rate herbicide application) and pesticide regulatory assessments.

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