# Use of near spectrometry in quantifying the spatial variability of soil characteristics and herbicide and 17β-estradiol sorption parameters at field scale

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### Introduction

An urgent need of the time is to meet the demands for food by the fast-growing world's population. According to the World Bank, the world population was estimated at around 7 billion in 2009. One approach in meeting food security is to increase the food production per unit area, for example, by using pesticides to reduce the risk of pre- and post-harvest losses of food to pests. Pesticides continue to be an integral part of successful agriculture production worldwide, with an estimated use of 35,000 tonnes per year in Canada alone.<sup>1</sup> Although there are many advantages to pesticide use, there are also concerns about their harmful effects on ecosystems and the quality of life on Earth.

A large portion of the pesticides applied to control pests in crops are entering soils and soil properties therefore strongly influence pesticide fate in the environment. The risk of pesticide movement from agricultural soils to the broader environment can be evaluated using pesticide fate models. A pesticide fate modeling approach also allows for preliminary testing of beneficial agricultural management strategies that reduce the movement of pesticides from agricultural soils to the broader environment.

One pesticide fate model is PRZM (Pesticide Root Zone Model, version 3.12.2) that is used as a policy tool for risk assessment of ground water contamination arising from pesticide use in Canadian agriculture. Sorption coefficients, termed K<sub>d</sub> values, are among the most sensitive input parameters in pesticide fate models and therefore their inaccurate determination leads to uncertainties in risk predictions.<sup>3</sup> The uncertainties associated with pesticide fate modeling at the large scale (field, regions) have been well documented and can be attributed to the lack of spatial data on pesticide sorption coefficients.<sup>2-4</sup> Regardless of the physico-chemical characteristics of the pesticide, the spatial and temporal variability of pesticide sorption coefficients is controlled by associated variations in soil properties, including soil organic carbon (SOC), pH and texture. Due to spatial variability of these soil properties in soil-landscapes and regions, it is still challenging to describe sorption coefficients statistically in large units. For example, conventional techniques such as batch-equilibrium experiments are relatively labour-intensive and expensive.

It has been well-documented that near infrared (NIR) spectroscopy is a useful tool for rapid determination of various soil properties (such as SOC%, pH and texture)<sup>5-6</sup> and we and others have found NIR spectroscopy to be useful for rapid determination of the sorption of pesticides by soil.<sup>7-8</sup> Hence, we hypothesize that NIR spectroscopy predictions can be used at the field level to better estimate statistical distributions of pesticide sorption coefficients in large units. Such knowledge could strengthen the versatility of pesticide fate models during the process of developing beneficial farm management strategies designed to improve pest control, while minimising the risk of pesticide off-site movement from an agricultural field.

Recent studies describe the application of pesticide fate models for also determining the fate and transport of natural steroidal estrogens in soil.<sup>9-10</sup> Natural steroidal estrogens, of which 17B-estradiol is the most potent, are produced and excreted by vertebrates including livestock. Livestock manure applied to agricultural land is one pathway by which such natural steroid estrogens can enter soils.

# **Materials and Methods**

### Research site and soil sampling

The study was conducted using soil samples from two hummocky terrains in Canada. One hummocky terrain consisted of two agricultural fields of the Manitoba Zero Tillage Research Association (MZTRA) in the province of Manitoba and the other consisted of one conventional tilled field, known as the St. Denis National Wildlife Research Area (SDNWA) in the province of Saskatchewan. The three fields were classified into seven landform elements using digital terrain models (grid size  $5x5m^2$ )<sup>11-14</sup> and, in each province, 10 soil profiles were collected from each of seven landform elements (Figure 1). In total, 314 soil samples were collected from MZTRA and 295 soil samples were collected from SDNWA. These samples represented each horizon of the total 140 soil profiles collected to 1 m depth (Figure 1).

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Soil samples were air-dried, sieved (<2 mm) and analysed for SOC, pH, and soil texture by employing a LECO CR-12 Carbon Analyser (LECO Corporation, Ontario, Canada), pH meter (Acumen 50 pH meter; Thermo Fisher, Texas, USA) and Horiba LA-950 laser particle size analyser (Horiba, California, USA), respectively. In addition, sorption studies to generate K<sub>d</sub> values of three herbicides (2,4-D, atrazine and glyphosate) and one estrogen (17β-estradiol) were conducted using the batch-equilibrium process,<sup>4</sup> whereby higher K<sub>d</sub> values indicate greater sorption per unit soil relative to smaller K<sub>d</sub> values.



Figure 1. Soil sampling positions at MZTRA (Field 1 and Field 2) and SDNWA (Field 3).

#### Near infrared spectroscopy

Spectra were obtained from 25 g of each air-dried and sieved (<2 mm) soil sample in a glass petri dish, using a 45VISNIR Corona (Carl Zeiss, Jena, Germany) spectrophotometer with a wavelength range of 380 to 1690 nm at 6 nm intervals (Figure 2A). Samples were also scanned on a Foss NIRSystems 6500 spectrophotometer equipped with a Rapid Content Sampler at a wavelength range of 1100 to 2500 nm at 2 nm intervals; samples were placed in a glass petri dish on the scanning window and rotated 120° between replicates (Figure 2B). All samples were scanned in triplicate on each instrument and the three spectra were averaged. Spectra were imported to The Unscrambler® (version 9.8, 2008; Camo Process ASA) and combined with reference data for calibration development. The spectral precision of both instruments was monitored by scanning three check samples after every 10 unknown samples. Both instruments provided very precise spectra but the Corona marginally outperformed the Foss 6500 when SD and CV% of the spectral data of all the check samples were compared at four wavelengths (Table 1).

Sample	45VISNIR Corona					Foss 6500			
		1186nm	1210nm	1410nm	1510nm	1186nm	1210nm	1410nm	1510nm
Check-1	Mean	0.5925	0.5802	0.4628	0.4367	0.6371	0.6263	0.5602	0.5091
n=13	SD	0.0034	0.0034	0.0032	0.0031	0.0030	0.0034	0.0032	0.0031
	CV%	0.5738	0.5860	0.6914	0.7099	0.4709	0.5429	0.5712	0.6089
Check-2	Mean	0.6181	0.6058	0.4898	0.4623	0.6661	0.6555	0.5908	0.5386
n=13	SD	0.0030	0.0029	0.0029	0.0028	0.0048	0.0048	0.0052	0.0054
	CV%	0.4854	0.4787	0.5921	0.6057	0.7206	0.7323	0.8802	1.0026
Check-3	Mean	0.6028	0.5917	0.4868	0.4588	0.6423	0.6326	0.5783	0.5254
n=13	SD	0.0028	0.0028	0.0032	0.0034	0.0049	0.0049	0.0048	0.0047
	CV%	0.4645	0.4732	0.6574	0.7411	0.7629	0.7746	0.8300	0.8946

Table 1. Spectral precision comparison of 45VISNIR Corona and Foss 6500 instruments using from MZTRA check samples.

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Partial least squares regression (PLS1) in The Unscrambler was used to develop calibrations for each constituent. The samples for each property or constituent were divided into calibration and validation data sets and calibrations were developed using the test set method. Before calibration development, the noisy region (340–700 nm) of the Corona spectra was removed before pre-treatments were performed on the raw spectral data. Wavelength ranges were 700–1690 nm for the Corona and 1100–2500 nm for the Foss 6500. Mathematical pre-treatments included smoothing over 5, 11, 21 and 41 wavelength points followed by transformation to first or second derivative. The best calibration for each parameter was selected based on the highest coefficient of determination  $(r^2)$ , lowest standard error of prediction (SEP) and high RPD value (ratio of SD of the validation set to SEP).<sup>15</sup> Values of RPD >4 are judged as indicating excellent calibrations, >3 are successful and between 2.25 and 3 are moderately successful. RER (ratio of range of validation set to SEP) values >10 are generally judged as moderately successful.<sup>16</sup>



Figure 2. NIR Spectra of MZTRA soil samples by Zeiss Corona (A) and Foss 6500 (B) instruments.

### **Results and Discussion**

The 609 soil samples demonstrated a very wide range of soil chemical and physical properties (Table 2). For example, landscape depressions in both MZTRA and SDNWA had a greater numerical amount of SOC than upper slope positions (on average). K<sub>d</sub> values of the herbicides 2,4-D and atrazine, and of 17β-estradiol were all very well correlated with SOC ( $r^2 > 0.80-0.90$ ) and these results are in agreement with other studies.<sup>17-20</sup> Hence, the K<sub>d</sub> values of these chemicals also appeared to be on average greater in depressions than upper slope positions. The sorption of 2,4-D, atrazine and 17β-estradiol decreased with increasing soil depth, possibly due to associated decreases in SOC. Other soil properties such as pH or soil texture showed weaker or no correlations with sorption of 2,4-D, atrazine and  $17\beta$ -estradiol. The effect of soil pH on sorption was not significant due to the alkaline to neutral range of pH within these landscapes as has previously been shown.<sup>2,18-19</sup> The herbicide glyphosate was not correlated with SOC nor with any other soil property, perhaps because the molecule has such exceptional affinity for being retained by the soil regardless of soil properties.<sup>21</sup> Therefore, the results of this study point to the well-established fact that some soil chemical

	MZTRA	A (N = 314)	SDNWA(N = 295)		
Constituent or Property	Range	Mean ± S.D.	Range	Mean ± S.D.	
K <sub>d</sub> _2,4-D (ml.g <sup>-1</sup> )	0.03-7.70	1.38 ± 1.53	0.01–5.11	$1.02 \pm 0.93$	
K <sub>d</sub> _Glyphosate (ml.g <sup>-1</sup> )	13.63-222.70	48.97 ± 26.96	5.36-842.01	78.10 ± 108.03	
K <sub>d</sub> _Atrazine (ml.g <sup>-1</sup> )	1.01–52.49	8.08 ± 8.47	0.08–9.12	2.19 ± 2.07	
K <sub>d</sub> _17β-Estradiol (ml.g <sup>-1</sup> )	8.28–58.71	24.26 ± 10.18	4.01–33.48	13.25 ± 6.09	
SOC%	0.42-5.81	1.99 ± 1.33	0.00-3.52	1.02 ± 0.96	
рН	6.93-8.54	$7.78 \pm 0.33$	6.52–9.37	8.18 ± 0.67	
Sand%	0.00–97.41	69.55 ± 15.70	9.25-87.32	48.17 ± 10.80	
Silt%	2.60-61.30	18.58 ± 8.36	9.28–76.14	40.77 ± 8.56	
Clay%	0.00-48.65	11.88 ± 8.94	0.00–30.6	11.06 ± 7.14	

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and physical properties, as well as some pesticide sorption coefficients, are spatially variable in soillandscapes. In addition, we demonstrate that a considerable spatial variability exists in hummocky landscapes for the sorption of  $17\beta$ -estradiol by soil.

For MZTRA, together with SOC, the K<sub>d</sub> values of herbicides 2,4-D and atrazine, as well as the estrogen 17β-estradiol, were successfully predicted by NIR spectroscopy using the Foss 6500 instrument whereas the prediction models for soil pH were weaker (Table 3). Good results were also produced with the Zeiss Corona instrument but the Foss 6500 instrument marginally outperformed the Corona. This was attributed to the larger wavelength range covered by the Foss 6500. Similarly, successful calibration results were obtained for SDNWA (Table 4) with the Foss 6500 also generally out-performing the Zeiss Corona instrument. Neither instrument was able to successfully predict the soil texture in hummocky landscapes. Calibration results were also poor for glyphosate, with low  $r^2$ , RPD and RER in both landscapes (Table 3 and 4).

		Foss 650		Corona-MZTRA				
Constituent	r²	SEP	RPD	RER	r <sup>2</sup>	SEP	RPD	RER
K <sub>d</sub> _2,4-D	0.92	0.39	3.96	17.24	0.88	0.51	3.02	14.91
K <sub>d</sub> _Glyphosate	0.54	16.91	1.4	6.97	0.41	19.19	1.34	8.41
K <sub>d</sub> _Atrazine	0.93	1.93	4.18	16.58	0.85	3.12	2.42	9.28
$K_d_17\beta$ -estradiol	0.92	2.71	3.78	14.77	0.93	2.69	3.75	15.27
SOC%	0.96	0.26	5.34	18.89	0.92	0.37	3.49	13.04
рН	0.67	0.19	1.70	8.22	0.76	0.16	2.08	9.18
Sand%	0.51	10.9	1.25	6.39	0.55	9.37	1.83	9.99
Silt%	0.43	5.51	1.35	7.17	0.49	5.20	1.64	10.6
Clay%	0.48	6.83	1.05	4.83	0.59	5.25	1.93	9.09

Table 3. Calibration results from Foss 6500 and Zeiss Corona instruments on MZTRA landscape.

Table 4. Calibration results from Foss 650	0 and Zeiss Corona instr	ruments on SDNWA landscape
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	Foss 6500-SDNWA				Corona-SDNWA			
Constituent	r <sup>2</sup>	SEP	RPD	RER	r <sup>2</sup>	SEP	RPD	RER
K <sub>d</sub> _2,4-D	0.86	0.34	2.53	11.4	0.82	0.38	2.22	10.03
K <sub>d</sub> _Glyphosate	0.59	60.44	1.76	9.01	0.57	56.22	1.90	9.68
K <sub>d</sub> _Atrazine	0.91	0.60	3.35	14.01	0.80	0.87	2.31	9.68
$K_d_17\beta$ -estradiol	0.84	2.42	2.53	10.89	0.81	2.58	2.37	10.21
SOC%	0.91	0.29	3.21	12.16	0.90	0.31	2.98	11.26
рН	0.65	0.39	1.71	6.55	0.76	0.33	2.05	7.83
Sand%	0.70	5.89	1.76	10.0	0.52	7.31	1.39	8.06
Silt%	0.51	5.92	1.44	9.03	0.41	6.59	1.29	8.12
Clay%	0.79	3.28	2.13	8.87	0.73	3.69	1.91	7.89

As well as high  $r^2$ , RPD and RER values, other parameters of successful calibration, such as low Standard Error of Prediction (SEP) and minimum bias, were also monitored during the calibration development. As an example, the NIR calibration results with Foss 6500 for SOC in Manitoba showed successful calibrations with low SEP (0.26) and low bias (3.89×10<sup>-7</sup>). Sand%, silt% and clay% properties for MZTRA and SDNWA soils showed RPD values of 2.1 or less with both instruments, which is lower than desirable for useful NIR prediction (Tables 3 and 4).

# Conclusion

NIR spectroscopy is a rapid and effective tool for predicting significant input parameters of pesticide fate models, including herbicide and natural steroidal estrogen sorption coefficients, where the sorption of these organic chemicals is strongly correlated to SOC. The calibration equations developed using NIR spectroscopy could be used to integrate NIR and PRZM for improving effective decision-making programmes such as those initiated by NAHARP (National Agri-Environmental Health Analysis and Reporting Programme), Canada. NIR spectroscopy demonstrated a high potential for use as a rapid and nonchemical technique for predicting soil organic carbon and K<sub>d</sub> values of 2,4-D, atrazine and 17β-estradiol. Nevertheless, glyphosate and soil textural properties were poorly predicted by NIR spectroscopy.

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