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

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

KEYWORDS: 17β-estradiol, near-infrared spectroscopy, soil organic carbon, soil profiles, sorption

INTRODUCTION

In 2006, a population of approximately 157 million livestock was reported in Canada,[1] producing millions of tons of manure every year. Livestock manure is an important source of nutrients for crop production when applied as fertilizer. Nevertheless, poor manure management strategies, especially overly high rates of application lead to environment contamination.[1] Loss of livestock manure containing steroid hormones, such as 17β-estradiol ((17β)-estra-1,3,5(10)-triene-3,17-diol), from manure-treated agricultural soils to water bodies has the potential to adversely affect the quality of fresh water sources.[2−6] A survey of 139 streamwater sources sampled across the United States revealed that 90% of the samples collected contained detectable levels of steroid hormone compounds,[7] which are most likely as a result of both agricultural and urban sources.[2,3,8] The presence of as low as 1 ng L^{-1} of 17β-estradiol in water has the potential to trigger feminization in male aquatic wildlife as well as to produce reproductive disorders in human males.[5]

Degradation of 17β-estradiol in soil is dependent on its chemical bioavailability that is reduced by the strong sorption of 17β-estradiol to soil constituents,[5,9] such as organic matter and silt.[10] 17β-Estradiol transport from soils to the broader environment by water is also limited by soil sorption.[11] Sorption coefficients of 17β-estradiol have been reported to be spatially variable across agricultural fields in ecoregions of Alberta, Canada.[12]

Risks of transport of pesticides and other organic contaminants, from soil to surrounding environments, can be assessed by models such as the Pesticide Root Zone model.[1,13,14] Casey et al.[10,15] describe the application of pesticide fate models for determining estrogen fate in soil. Examples of input parameters for fate models are the physicochemical properties of pesticides or estrogens, including sorption coefficients; weather data, including rainfall and temperature; soil-landscape characteristics, including terrain attributes; and management practices.[1,14] The uncertainties associated with fate modeling at the large scale are particularly due to the lack of pertinent data on the spatial variation of pesticide or estrogen sorption coefficients in soil landscapes and regions.[16] Generating quality input parameters rapidly and cost effectively may strengthen the versatility and reliability of chemical fate models when developing beneficial farm management strategies for manure management in agricultural fields. Wet chemistry methods, such as the batch-equilibrium process, are generally adopted for determining sorption coefficients (K_d) of organic molecules.[17] Such techniques not only are expensive and time-consuming but often employ hazardous radiolabeled chemicals.[18−20] To reduce the uncertainties in risk assessments, efficient methods are needed that are cost-effective, rapid, and reliable but also generate quality data to determine spatial distributions of sorption coefficients in soil landscapes.

Near-infrared spectroscopy (NIRS) has been shown since the 1980s to provide rapid, cost-effective, and accurate determination of soil properties.[21] Total or fractions of carbon

Table 1. Constituents in the 609 Soil Samples from the MZTRA and SDNWA Sites[a]

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

[a]Values are mean ± SD. The K_d values are given for 17β-estradiol.

have been predicted in soils from Canada,[22,23] United States,[24−26] and Uruguay.[27] Carbon, nitrogen, and phosphorus have been predicted in agricultural soils from China.[28] Clay content has been predicted in Danish soil.[29] Bengtsson et al.[30] and Forouzangohar et al.[20] reported successful prediction of pesticide sorption coefficients of lindane and diuron in agricultural soils collected from different parts of Sweden and Australia. Kookana et al.[31] successfully predicted K_d values of the herbicide atrazine in Australian soils. The objectives of this study were to determine the feasibility of NIRS as a rapid tool to quantify the spatial variability of soil properties and 17β-estradiol sorption coefficients in the soil profiles of irregular undulating to hummocky terrain landscapes of Canada.

■ MATERIALS AND METHODS

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

At both MZTRA and SDNWA sites, 10 soil profiles of 1 m depth were collected from each of 7 landform elements, including convergent or divergent shoulders, convergent or divergent backslopes, convergent or divergent footslopes, and depressions. The landform element classification was performed using Digital Elevation models with a 5 × 5 m² grid and the landform segmentation technique described by Pennock and colleagues.[32,33] Soil profiles were collected with a truck-mounted hydraulic probe, 5 cm in diameter. The Canadian System of Soil Classification (CSSC 1998) was used to classify the soil profiles into A, B, and C horizons. Examples of horizons are Ap, Ah (A horizons), Bg, Bm, Bmk (B horizons), and Cca, Ck (C horizons). Each horizon was treated as a separate soil sample. A total of 609 soil samples from MZTRA (n = 314) and SDNWA (n = 295) landscapes were collected.

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

17β-Estradiol Sorption Analysis. 17β-Estradiol of 99% chemical purity, 6,7-³H(N), 99% radiochemical purity, and specific activity of 13.51×10^{-10} Bq mmol⁻¹ (American Radiolabeled Chemicals Inc., St. Louis, MO, USA) was used in batch-equilibrium experiments as described by Caron et al.[12] These experiments were used to quantify

the K_d values of 17β-estradiol for each soil sample. All soil samples, glassware, and deionized water used for stock solution preparation were sterilized by autoclaving at 121 °C for 30 min to minimize the risk of 17β-estradiol degradation during the batch experiment.[12] Preliminary batch experiments revealed that the equilibrium time of 24 h was appropriate for sorption analysis of 17β-estradiol. 17β-Estradiol stock solutions with a specific activity of 16.70 Bq mL⁻¹ were prepared by dissolving both analytical grade and radiolabeled 17β-estradiol in 0.01 M CaCl₂ solution. A 17β-estradiol stock solution of 10 mL volume was added to 5 g of soil in 50 mL glass tubes in duplicates and rotated in the dark for 24 h under controlled temperature conditions of 5 °C to achieve equilibrium between the concentration of 17β-estradiol sorbed by soil (C_s in g kg⁻¹) and the concentration of 17β-estradiol remaining in solution (C_e g L⁻¹). Samples were centrifuged at 10,000 rpm for 10 min. Then, 1 mL supernatant aliquots were transferred to scintillation vials (duplicates) containing 5 mL of scintillation cocktail. After 24 h in the dark, scintillation vials were counted in a Beckman liquid scintillation counter (LSC) (LS 7500 Beckman Instruments, Fullerton, CA, USA) with automated quench correction using the #H method for determining remaining radioactivity in the samples. The sorption partitioning coefficients (K_d) were determined as $K_d = C_s/C_e$.

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

Spectra for each instrument/sample holder combination were imported into the Unscrambler multivariate statistic analysis software version 9.8 (2008, CAMO Process ASA). Triplicate spectra for each sample were averaged, and the reference data for each sample were added before calibration development. Spectral precision of both instruments was monitored by scanning the same three check samples after every 10 unknown samples. Although the samples stored in the vials were scanned more rapidly than those in Petri dishes, the Petri dishes provided a more optically uniform interface and larger area of sample scanned than did the vials. The noisy region (380−700 nm) of the Corona spectra was removed before mathematical pretreatments were performed on the raw spectral data of Petri dishes. Wavelength ranges were thus 700−1690 nm for the Corona and 1100−2500 nm for the Foss 6500 instrument. Partial least squares regression (PLS1) in the Unscrambler software was used to develop calibrations for each property/constituent. Calibrations were developed using the test set method in which all the samples were sorted from low to high for each property or constituent and were divided into calibration (two-thirds of the total samples) and validation (one-third of the total samples) sets by selecting every third sample for the validation set. Consequently, the range of values for each property or constituent was approximately the same in the calibration file and the corresponding validation file. A total of 37 calibration trials were

made for every property or constituent by performing mathematical pretreatments on raw spectra by smoothing over 5, 11, 21, or 41 wavelength points followed by transformation to the first or second derivative and using derivative gaps of 5, 11, 21, or 41 wavelength points. Wavelength points were 2 nm apart. The best calibration for each parameter was selected based on the highest coefficient of determination (r^2), the lowest standard error of prediction (SEP), and the highest ratio of standard error of prediction to standard deviation (RPD) value. The RPD value is the ratio of SD of the constituent values in the validation set to the SEP.[34] In environmental samples, values of RPD >4 are judged as indicating excellent calibrations, >3 are successful, and between 2.25 and 3.0 are moderately successful. In addition, the ratio of range of validation set to SEP (RER) values was also considered with RER values of greater than 10 generally being judged as moderately successful.[35,36]

■ RESULTS AND DISCUSSION

The 609 soil samples collected from A, B, and C horizons of the 140 soil profiles demonstrated widely ranging soil properties and 17β-estradiol K_d values (Table 1). The 17β-estradiol K_d values in MZTRA ranging 8.28−58.71 L kg^{-1} and those in SDNWA ranging 4.01−33.48 L kg^{-1} (Table 1) were significantly ($p < 0.001$) positively correlated with SOC and significantly ($p < 0.001$) negatively correlated with soil pH and clay content (Table 2). Mean SOC and mean 17β-estradiol K_d

Table 2. Pearson Correlation Coefficients (r) among 17β-Estradiol (K_d Values) and Soil Properties in MZTRA and SDNWA[a]

site	constituent or property	SOC %	pH	sand %	silt %	clay %
MZTRA	17β-estradiol	0.79[b]	−0.58[b]	0.18[b]	NS	−0.28[b]
	SOC %		−0.62[b]	0.19[b]	NS	−0.33[b]
	pH			−0.25[b]	NS	0.37[b]
	sand %				−0.90[b]	−0.91[b]
	silt %					0.65[b]
SDNWA	17β-estradiol	0.81[b]	−0.24[b]	0.35[b]	NS	−0.60[b]
	SOC %		−0.40[b]	0.38[b]	NS	−0.65[b]
	pH			NS	−0.32[b]	0.25[b]
	sand %				−0.75[b]	−0.61[b]
	silt %					NS

[a]NS: correlation is not significant at the 0.05 level. [b]Correlation is significant at the 0.001 level.

values decreased from A > B > C horizon, while mean soil pH and mean clay content increased with soil depth (Table 1). Under zero-tillage management practices at MZTRA, soils contained on average two times greater SOC and 17β-estradiol

K_d values than the conventional-tillage soils at SDNWA (Table 1).

Both NIRS instruments demonstrated satisfactory spectral precision, although the Corona marginally outperformed the Foss 6500 instrument when the coefficient of variation of the spectra of three check samples were compared at four wavelengths points (1186, 1210, 1410, and 1510 nm) (Table 3). The soil spectra displayed absorbance peaks at three major wavelength points, that is, 1400, 1900, and 2200 nm, related to O−H bonds of hygroscopic water present in the air-dried soil samples (Figure 1). Average spectra of samples from the A, B,
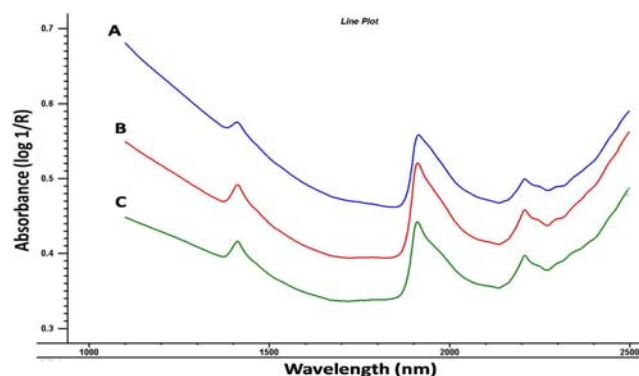

Figure 1. Spectra of soil samples from the A, B, and C horizons in MZTRA recorded by the Foss 6500.

and C horizons in MZTRA (and SDNWA, data not shown) were distinctively different in absorbance values (Figure 1). This is reflected in clustering of samples from A (mean SOC = 3.41), B (mean SOC = 1.37) and C (mean SOC = 0.94) horizons in MZTRA (and SDNWA, data not shown) in the principal component analysis, reflecting differences in SOC and average particle size in the respective horizons (Figure 2).

Regardless of the site location and instrument, successful to moderately successful calibration results were obtained for K_d values of 17β-estradiol and for SOC. Calibrations for soil pH and clay content were judged to be useful. Results for soil samples scanned in Petri dishes with the Foss 6500 instrument demonstrated the most successful results in MZTRA ($r^2 = 0.92$; RPD = 3.78) when the spectra (1100−2498 nm) were smoothed over 11 wavelength points, using the second derivative (Figure 3A, Table 4), where 96% of the variance in the measured 17β-estradiol K_d values was explained by the first principal component. Similarly, in the SDNWA soil landscape, the Foss 6500 successfully predicted 17β-estradiol with r^2 of

Table 3. Spectral Precision Comparison of Zeiss Corona and Foss 6500 Instruments Using Check Sample Means (Absorbance log 1/R) in Petri Dishes

|		Zeiss Corona				Foss 6500			
sample		1186 nm	1210 nm	1410 nm	1510 nm	1186 nm	1210 nm	1410 nm	1510 nm
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
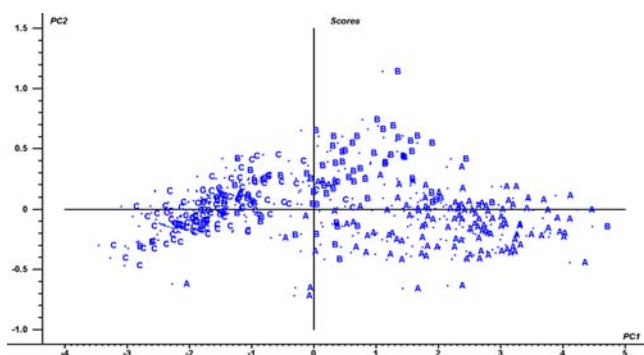
Figure 2. Scores plot from principle component analysis of 314 soil samples of MZTRA belonging to A, B, and C horizons using spectra recorded by the Foss 6500.

0.84 and RPD of 2.53 (Table 4). Comparatively, the Foss 6500 marginally outperformed the Corona (r^2 = 0.81; RPD = 2.37) in SDNWA, and the differences between the two instruments were even smaller for MZTRA (Table 4).

This was the first study to explore the feasibility of NIRS application for landscape-scale quantification of 17β-estradiol K_d values in soil. Nevertheless, infrared spectroscopy has successfully been applied to estimate sorption coefficients for other organic chemicals (pesticides) in agricultural soils at the regional scale in Sweden[30] and Australia.[20,31]

Excellent calibration results were obtained for SOC by the Foss 6500 in the MZTRA (r^2 = 0.96; RPD = 5.34), and a successful calibration was obtained in the SDNWA (r^2 = 0.91; RPD = 3.21) (Figure 3B, Table 4). Comparatively, the Foss 6500 marginally outperformed the Corona for both MZTRA and SDNWA (Table 4). The results of the present study support results of previous studies,[22−25,27,29,36−38] all of which researchers successfully determined the content of carbon fractions in soils by NIRS. Moderately useful calibrations were developed for soil pH in MZTRA (r^2 = 0.76; RPD = 2.08) and SDNWA (r^2 = 0.76; RPD = 2.05) with the Corona (Figure 3C, Table 4). Soil clay was moderately usefully predicted by the Foss 6500 in SDNWA (r^2 = 0.79; RPD = 2.13), but the results were relatively poor for clay by Corona (r^2 = 0.73; RPD = 1.91) and by either instruments in MZTRA (Figure 3D, Table 4). Soil sand and silt contents were not successfully predicted by either instrument (Table 4).

The present study demonstrated that NIRS is a rapid and cost-effective technology that could be used efficiently to estimate sorption coefficients of 17β-estradiol, together with some soil properties. It is thus a promising substitute for some costly and time-consuming conventional wet chemistry techniques. The data so generated by NIRS can readily be used as input parameters in the chemical fate models for efficient risk assessments and effective decision making programs for environmental safety. Although both instruments successfully demonstrated the feasibility of predicting 17β-estradiol K_d values along with SOC, pH, and clay content in air-dried and sieved soil samples, the most effective use of NIRS technology will be in generating on-site data from field-moist soil. This explains why field portable instruments such as the Corona are receiving increased attention in carbon monitoring and environmental studies.[22,23,34,37,38] Field portable instruments, such as the Corona, have the advantage of further decreasing costs associated with sample collection, handling, and storage and may provide a quick on-site assessment of the chemical properties of field-moist samples.
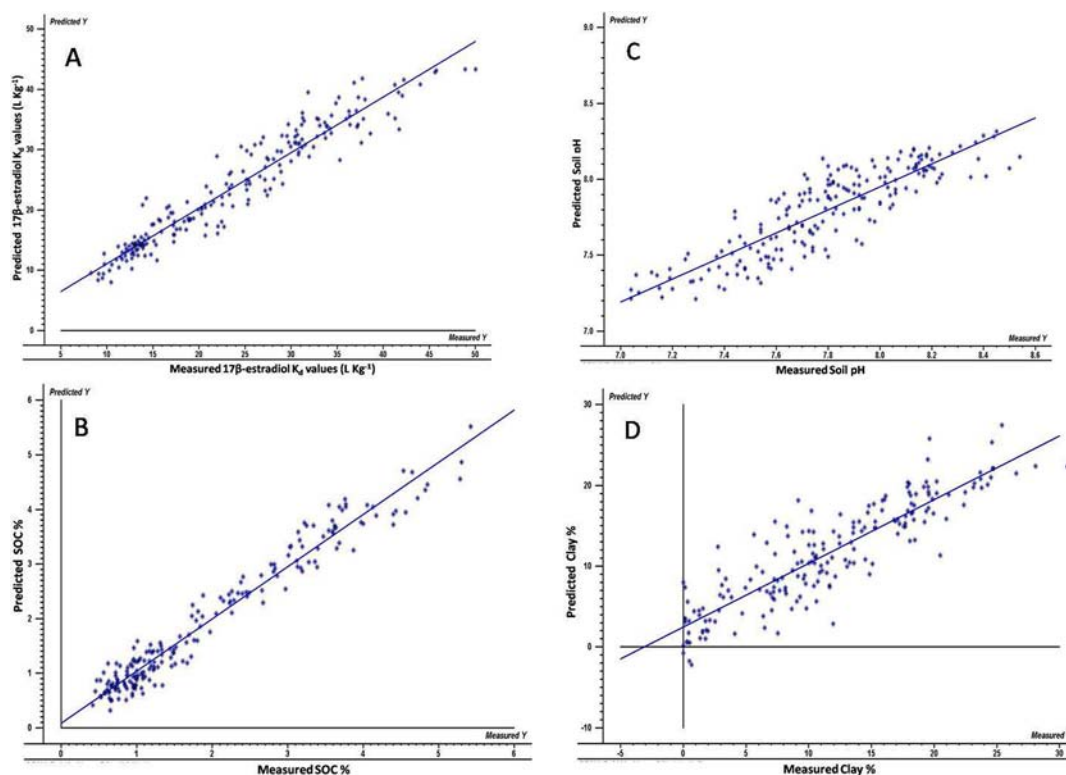

Figure 3. Linear regression relationship between NIR-predicted and measured values for sorption coefficients of 17β-estradiol (A), soil organic carbon (B), soil pH (C), and soil clay (D).

Table 4. Calibration Results of 17β-Estradiol (K_d Values) and Soil Properties on MZTRA and SDNWA Soil Samples Presented in Petri Dishes to the Foss 6500 and the Zeiss Corona[a]

MZTRA	calibration	r^2	SEP	bias	RPD	RER	math treatment
Foss 6500	17β-estradiol	0.92	2.71	8.75×10^{-7}	3.78	14.77	s11e5
	SOC %	0.96	0.26	3.89×10^{-7}	5.34	18.89	s5e5
	pH	0.67	0.19	2.76×10^{-6}	1.70	8.22	s5e5
	sand %	0.51	10.9	5.48×10^{-6}	1.25	6.39	s5e11
	silt %	0.43	5.51	-6.90×10^{-5}	1.35	7.17	s41e5
	clay %	0.48	6.83	4.12×10^{-6}	1.05	4.83	s5e5
Corona	17β-estradiol	0.93	2.69	8.06×10^{-5}	3.75	15.27	s5e5
	SOC %	0.92	0.37	2.14×10^{-8}	3.49	13.04	s21e41
	pH	0.76	0.16	-1.80×10^{-7}	2.08	9.18	s5e41
	sand %	0.55	9.37	7.41×10^{-5}	1.83	9.99	s5e5
	silt %	0.49	5.2	-4.03×10^{-5}	1.64	10.6	s11e5
	clay %	0.59	5.25	-1.20×10^{-5}	1.93	9.09	s11e11

SDNWA	calibration	r^2	SEP	bias	RPD	RER	math treatment
Foss 6500	17β-estradiol	0.84	2.42	-4.42×10^{-7}	2.53	10.89	s41d21
	SOC %	0.91	0.29	-1.86×10^{-6}	3.21	12.16	s5e5
	pH	0.65	0.39	-2.32×10^{-5}	1.71	6.55	s41e5
	sand %	0.70	5.89	-8.01×10^{-6}	1.76	10.00	s5e11
	silt %	0.51	5.92	1.36×10^{-4}	1.44	9.03	s41e5
	clay %	0.79	3.28	-6.04×10^{-5}	2.13	8.87	s5e5
Corona	17β-estradiol	0.81	2.58	-6.99×10^{-7}	2.37	10.21	s5e5
	SOC %	0.90	0.31	-5.60×10^{-8}	2.98	11.26	s41e41
	pH	0.76	0.33	-2.88×10^{-7}	2.05	7.83	s5e21
	sand %	0.52	7.31	2.22×10^{-5}	1.39	8.06	s41d5
	silt %	0.41	6.59	3.24×10^{-5}	1.29	8.12	s5e5
	slay %	0.73	3.69	-7.35×10^{-6}	1.91	7.89	s41d11

[a] r^2 = coefficient of determination; SEP = standard error of prediction; bias = difference between mean of the NIR-predicted data and the reference data; RPD = ratio of standard deviation of values in the validation set to SEP; RER = ratio of range of values in the validation set to SEP; segment = number of wavelength points over which the spectra were smoothed and designated as "s"; gap = number of wavelength points over which the derivative was calculated and designated as "d" for the first derivative and "e" for the second derivative.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) *Environmental Sustainability of Canadian Agriculture*; Agri-Environmental Indicator Report Series, Report No. 3; Eilers, W., MacKay, R., Graham, L., Lefebvre, A., Eds.; Agriculture and Agri-Food Canada: Ottawa, Ontario, 2010.

(2) Nichols, D. J.; Daniel, T. C.; Moore, P. A., Jr.; Edwards, D. R.; Pote, D. H. Runoff of estrogen hormone 17 beta-estradiol from poultry litter applied to pasture. *J. Environ. Qual.* **1997**, 26 (4), 1002–1106.

(3) Nichols, D. J.; Daniel, T. C.; Edwards, D. R.; Moore, P. A., Jr; Pote, D. H. Use of grass filter strips to reduce 17 beta-estradiol in runoff from fescue-applied poultry litter. *J. Soil Water Conserv.* **1998**, 53, 74–77.

(4) Peterson, E. W.; Davis, R. K.; Orndorff, H. A. 17β-Estradiol as an indicator of animal waste contamination in mantled karst aquifers. *J. Environ. Qual.* **2000**, 29 (3), 826–834.

(5) Colucci, M. S.; Henry, B.; Topp, E. Persistence of estrogenic hormones in agricultural soils: 1. 17β-Estradiol and estrone. *J. Environ. Qual.* **2001**, 30, 2070–2076.

(6) Ying, G. G.; Kookana, R. S.; Ru, Y. J. Occurrence and fate of hormone steroids in the environment. *Environ. Int.* **2002**, 28, 545–551.

(7) Koplin, D. W.; Furlong, E. T.; Meyer, M. T.; Thruman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H. T. Pharmaceuticals, hormones, and other organic waste water contaminents in U.S. streams, 1999–2000; a national reconnaissance. *Environ. Sci. Technol.* **2002**, 36, 1201–1211.

(8) Kinney, C. A.; Furlong, E. T.; Zaugg, S. D.; Burkhardt, M. R.; Werner, S. L.; Cahill, J. D.; Jorgensen, G. R. Survey of organic wastewater contaminants in biosolids destined for land application. *Environ. Sci. Technol.* **2006**, 40, 7207–7215.

(9) Hanselman, T. A.; Graetz, D. A.; Wilkie, A. C. Manure-borne estrogens as potential environmental contaminants: A review. *Environ. Sci. Technol.* **2003**, 37 (24), 5471–5478.

(10) Casey, F. X. M.; Larsen, G. L.; Hakk, H.; Šimůnek, J. Fate and transport of 17β-estradiol in soil-water systems. *Environ. Sci. Technol.* **2003**, 37, 2400–2409.

(11) Colucci, M. S.; Topp, E. Dissipation of part-per-trillion concentrations of estrogenic hormones from agricultural soils. *Can. J. Soil Sci.* **2001**, 82, 335–340.

(12) Caron, E.; Farenhorst, A.; Zvomuya, F.; Gaultier, J.; Rank, N.; Goddard, T.; Sheedy, C. Sorption of four estrogens by surface soils from 41 cultivated fields in Alberta. *Geoderma* **2010**, 155, 19–30.

(13) Carsel, R. F.; Imhoff, J. C.; Hummel, P. R.; Cheplick, J. M.; Donigan, A. S. J. *PRZM-3. A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: User Manual for Release 3.0*; National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency: Athens, Georgia, 1998.

(14) Cessna, A. J.; Sheedy, C.; Farenhorst, A.; McQueen, D. A. R. The Canadian indicator of risk of water contamination by pesticides. In *Environmental Sustainability of Canadian Agriculture*; Agri-Environmental Indicator Report Series, Report No. 3; Lefebvre, A., Eilers, W., Chunn, B., Eds.; Agriculture and Agri-Food Canada: Ottawa, Ontario, 2010; pp 101−107.

(15) Casey, F. X. M.; Šimůnek, J.; Lee, J.; Larsen, G. L.; Hakk, H. Sorption, mobility, and transformation of estrogenic hormones in natural soils. *J. Environ. Qual.* **2005**, *34*, 1372−179.

(16) Dubus, I. G.; Brown, C. D.; Beulke, S. Sensitivity analyses for four pesticide leaching models. *Pest Manage. Sci.* **2003**, *59*, 962−982.

(17) Wauchope, R. D.; Yeh, S.; Linders, J. B.; Kloskowski, R.; Tanaka, K.; Rubin, B.; Katayama, A.; Kordel, W.; Gerstl, Z.; Lane, M.; Unsworth, J. B. Pesticide soil sorption parameters: Theory, measurement, uses, limitations and reliability. *Pest Manage. Sci.* **2002**, *58* (5), 419−445.

(18) Williams, P. C. Implementation of near-infrared technology. In *Near-Infrared Technology in the Agriculture and Food Industries*, 2nd ed.; Williams, P., Norris, K., Eds.; American Association of Cereal Chemists: St. Paul, MN, 2001; pp 145−169.

(19) Williams, P. *Near-Infrared Technology-Getting the Best Out of Light: A Short Course in the Practical Implementation of Near-Infrared Spectroscopy for the User*, 5.4 ed.; PDK Grain, PDK Projects, Inc.: Canada, 2009.

(20) Forouzangohar, M.; Cozzolino, D.; Kookana, R. S.; Smernik, R. J.; Forrester, S. T.; Chittleborough, D. J. Direct comparison between visible near- and mid-infrared spectroscopy for describing diuron sorption in soils. *Environ. Sci. Technol.* **2009**, *43* (11), 4049−4055.

(21) Haaland, D. M.; Thomas, V. T. Partial least-squares methods for spectral analyses. 1. Relation to other quantitative calibration methods and the extraction of qualitative information. *Anal. Chem. J.* **1988**, *60*, 1193−1202.

(22) Malley, D. F.; Martin, P. D.; McClintock, L. M.; Yesmin, L.; Eilers, R. G.; Haluschak, P. Feasibility of analyzing archived Canadian prairie agricultural soils by near infrared reflectance spectroscopy. In *Near-Infrared Spectroscopy*, Proceedings of the 9th International Conference; Davies, A. M. C., Giangiacomo, R., Eds.; NIR Publications: Norwich, UK, 2000; pp 579−585.

(23) Martin, P. D.; Malley, D. F.; Manning, G.; Fuller., L. Determination of soil organic carbon and nitrogen at the field level using near-infrared spectroscopy. *Can. J. Soil Sci.* **2002**, *82*, 413−422.

(24) Chang, C. W.; Laird, D. A. Near-infrared reflectance spectroscopic analysis of soil C and N. *Soil Sci.* **2002**, *167*, 110−116.

(25) McCarty, G. W.; Reeves, J. B., III; Reeves, V. B.; Follett, R. F.; Kimble, J. M. Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. *Soil Sci. Soc. Am. J.* **2002**, *66*, 640−646.

(26) Reeves, J. B., III; McCarty, G. W.; Mimmo, T. The potential of diffuse reflectance spectroscopy for the determination of carbon inventories in soil. *Environ. Pollut.* **2002**, *116*, S277−S284.

(27) Cozzolino, D.; Moron, A. Potential of near-infrared reflectance spectroscopy and chemometrics to predict soil organic carbon fractions. *Soil Tillage Res.* **2006**, *85*, 78−85.

(28) He, Y.; Song, H.-y.; Pereira, A. G.; Gomez, A. H. Measurement and analysis of soil nitrogen and organic matter content using near-infrared spectroscopy techniques. *J. Zhejiang Univ., Sci.* **2005**, *6B* (11), 1081−1086.

(29) Sorensen, L. K.; Dalsgaard, S. Determination of clay and other soil properties by near infrared spectroscopy. *Soil Sci. Soc. Am. J.* **2005**, *69*, 159−167.

(30) Bengtsson, S.; Berglof, T.; Kylin, H. Near infrared reflectance spectroscopy as a tool to predict pesticide sorption in soil. *Bull. Environ. Contam. Toxicol.* **2007**, *78*, 295−298.

(31) Kookana, R. S.; Janik, L. J.; Forouzangohar, M.; Forrester, S. T. Prediction of atrazine sorption coefficients in soils using mid-infrared spectroscopy and partial least-squares analysis. *J. Agric. Food Chem.* **2008**, *56*, 3208−3213.

(32) Pennock, D. J.; Zebarth, B. J.; DeJong, E. Landform classification and soil distribution in the hummocky terrain, Saskatchewan, Canada. *Geoderma* **1987**, *40*, 297−315.

(33) Pennock, D. J. Terrain attributes, landform segmentation, and soil redistribution. *Soil Tillage Res.* **2003**, *69*, 15−26.

(34) Williams, P. C. Variables affecting near-infrared reflectance spectroscopic analysis. In *Near-Infrared Technology in the Agricultural and Food Industries*; Williams, P., Norris, K., Eds.; American Association of Cereal Chemists: St. Paul, MN, 1987; pp 143−167.

(35) Starr, C.; Morgan, A. G.; Smith, D. B. An evaluation of near-infrared reflectance analysis in some plant-breeding programmes. *J. Agric. Sci.* **1981**, *97*, 107−118.

(36) Malley, D. F.; Martin, P. D.; Ben-Dor, E. Application in analysis in soils. In *Near-Infrared Spectroscopy in Agriculture*; Roberts, C. A., Workman, J., Jr., Reeves, J. B., III, Eds.; American Society of Agronomy, Inc.: Madison, WI, **2004**; Ch 26, pp 729−784.

(37) Vasques, G. M.; Grunwald, S.; Sickman, J. O. Modeling of soil organic carbon fractions using visible-near-infrared spectroscopy. *Soil Sci. Soc. Am. J.* **2009**, *73*, 176−184.

(38) Sudduth, K. A.; Hummel, J. W. Soil organic matter, CEC, and moisture sensing with a portable NIR spectrophotometer. *Trans. ASAE* **1993**, *36*, 1571−1582.