

1 **Near-infrared spectroscopy as a tool for generating sorption input parameters for pesticide**
2 **fate modeling**

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30 **ABSTRACT**

31 Sorption parameters (such as K_d values) are among the most sensitive input parameters in
32 pesticide fate models. This study demonstrates that near-infrared spectroscopy (NIRS), in
33 combination with batch equilibrium techniques, can be used to estimate K_d values, thereby
34 increasing throughput of the many samples required to characterize spatial variability of
35 pesticide sorption within fields. The Pesticide Root Zone Model (v. 3.12.2) was used to compare
36 scenarios that used NIRS spectral data, pedotransfer functions and batch equilibrium methods as
37 inputs for the calculation of 2,4-D and atrazine leaching in 591 soil horizons. Based on the 3,564
38 simulation runs conducted, we concluded that the added benefit of NIRS is most useful when the
39 pesticides under study have small sorption potentials and short half-lives in soil. 2,4-D and
40 atrazine sorption by soil was highly correlated to soil organic carbon content (SOC) in the fields
41 under study. The feasibility of using NIRS to predict pesticide K_d values largely relies on the
42 sorption of the pesticide being significantly correlated to SOC. In addition, successful regional
43 approaches to predicting K_d values from NIRS spectral data can also be developed when the
44 calibration model is derived by combining a set of fields where each has a similar statistical
45 population characteristic in K_d values.

46

47 **Key Words:** 2,4-D, Atrazine, Leaching, Near-Infrared Spectroscopy, Pesticide Root Zone
48 Model, Sorption.

49

50 INTRODUCTION

51 Sorption parameters (K_d values) are among the most sensitive input parameters in pesticide fate
52 models used to calculate pesticide transport to depth (Boesten and Van der Linden 1991,
53 Villeneuve et al. 1998, Dubus et al. 2003a, Dubus et al. 2003b, Farenhorst et al. 2009). There are
54 large variations in sorption parameters within and between agricultural fields. For example, for
55 the herbicide 2,4-D in surface soils, its sorption parameter K_d ranged from 0.56 to 12.5 L/kg
56 ($n=72$) along a 360-m long transect in a single field and from 0.6 to 14.5 L/kg ($n=41$) across
57 fields spanning a 660,000 km² area (Gaultier et al. 2006, Gaultier et al. 2008). Because sorption
58 parameters are seldom quantified in sufficient spatial detail within and between simulation units
59 (Huber et al. 2000, Gagnon et al. 2014), there have been large uncertainties in risk assessments,
60 regardless of the pesticide fate model used (Dubus et al. 2003b, Dann et al. 2006, Farenhorst et
61 al. 2009).

62

63 To reduce uncertainties in large-scale risk assessments, efficient methods are needed that can
64 rapidly, and inexpensively, estimate sorption parameters for a large number of samples. The
65 sorption of a pesticide is dependent on soil characteristics (MacKay and Vasudevan 2012) and so
66 pesticide K_d values are usually assigned to simulation units by applying pedotransfer functions to
67 soil geographical databases. Weber et al. (2004) established pedotransfer functions to calculate
68 K_d values for a wide range of non-ionic or ionizable pesticides, with equations based on up to
69 three soil properties that were the most consistently reported in soil geographical databases: soil
70 organic carbon content (SOC), soil pH and clay content.

71

72 Near-infrared spectroscopy (NIRS) can be used to estimate one or more soil properties from
73 spectral data, including SOC, soil pH, clay content, carbonate content, cation exchange capacity,
74 as well as aluminum and iron concentrations in minerals (Ben-Dor and Banin 1990a, Ben-Dor
75 and Banin 1990b, Malley et al. 2000, Chang and Laird 2002, Martin et al. 2002, Sorensen and
76 Dalsgaard 2005, Singh et al. 2012). These soil properties play an important role in the sorption of
77 pesticide chemical structures (MacKay and Vasudevan 2012) and so NIRS could be used to
78 rapidly estimate pesticide K_d values from spectral data. For fields and regions, NIRS has been
79 previously used to estimate the sorption of nonionic (lindane, linuron) (Bengtsson et al. 2007)
80 and ionizable (atrazine and 2,4-D) (Singh et al. 2010) pesticides in soils. Similarly, mid-infrared
81 spectroscopy has been successfully used to estimate the sorption of atrazine (Kookana et al.
82 2008) and the nonionic pesticide, diuron (Forouzangohar et al. 2008) in soils. However, no study
83 has integrated the use of infrared spectroscopy with pesticide fate models and hence the impact
84 of estimating sorption input parameters by infrared spectroscopy on calculated pesticide
85 transport is unknown.

86
87 In this study, the base (or reference) scenario for calculating downward vertical pesticide
88 transport consisted of using K_d values measured in the laboratory by batch equilibrium
89 experiments. The measured K_d values were used for input in the Pesticide Root Zone Model
90 version 3.12.2 (PRZM-3) (Carsel et al. 1998) which is an extensively validated model used by
91 both European and North American governments to assess the risk of water contamination by
92 pesticides in fields and regions (Dubus et al. 2003a, Gaultier et al. 2008, Cessna et al. 2010,
93 Water Models). The objective of this study was to compare the base scenario with scenarios that

94 used NIRS spectra or pedotransfer functions (see Weber et al. 2004) as inputs for estimating K_d
95 values and leaching estimates using PRZM-3.

96

97 **MATERIAL AND METHODS**

98 **Soil samples and characteristics.** This study utilized 591 soil samples collected from two
99 irregular undulating to hummocky terrains in the Canadian Prairies. Sites were a 16-ha zero-
100 tilled agricultural area at the Manitoba Zero Tillage Research Association research farm (49°
101 53'N latitude, 99° 58'W longitude) near Brandon, Manitoba, Canada, and a 20-ha
102 conventionally-tilled area at the St. Denis National Wildlife Association (52° 12'N latitude, 106°
103 5'W longitude) near Saskatoon, Saskatchewan, Canada. Both the Manitoba and Saskatchewan
104 fields were mapped (grid size 5x5 m²) using digital terrain modeling software (Pennock 2003) to
105 identify seven landform elements in which soil profiles were sampled. Landform elements were
106 convergent and divergent shoulders, convergent and divergent backslopes, convergent and
107 divergent footslopes, and depressions, with the general topography and soil profile sampling
108 locations presented in Figure S1 (Supplementary Information). Soil profiles were sampled to 1 m
109 depth by horizon in 70 locations at both sites using a truck mounted 5 cm diameter hydraulic
110 probe. The 307 soil samples collected from Manitoba were from 23 different horizons. The 284
111 soil samples collected from Saskatchewan were from 22 different horizons. The ranges in
112 %SOC, soil pH, %sand, %silt, and %clay at both the Manitoba and Saskatchewan fields are
113 presented in Table S1 (Supplementary Information).

114

115 **Near-Infrared Spectroscopy (NIRS) and batch equilibrium data.** Near-Infrared spectra were
116 recorded for each horizon using a 25 g subsample and the Foss NIRS Systems model 6500

117 spectrophotometer (Carl Zeiss, Jena, Germany) equipped with a rapid content sampler. Soil was
118 presented in 5 cm diameter glass petri dishes to collect data over the wavelength range of 1100 to
119 2500 nm at 2 nm intervals, which resulted in 700 absorbance values for each spectrum. Triplicate
120 spectra were obtained for each sample by rotating the petri dish 120 degrees between scans.
121 Subsamples of horizons were also analyzed for soil properties (%SOC, soil pH, %clay, %silt and
122 %sand) as well as for 2,4-D and atrazine K_d values. Those results have been previously
123 published (Singh et al. 2014). K_d values were determined by batch equilibrium experiments
124 using 50 mL Teflon tubes containing 5 g soil and 10 mL of either a 2,4-D or atrazine solution
125 prepared in 0.01 M CaCl_2 at a concentration of 1 mg herbicide/L. K_d value (L/kg) was calculated
126 using C_s/C_e , where C_s is the amount of chemical sorbed on the soil at equilibrium (g/kg), and C_e
127 is the amount of chemical remaining in the solution at equilibrium (g/L). Throughout this paper,
128 the 2,4-D and atrazine K_d values determined in the laboratory by batch-equilibrium experiments
129 will be referred to as LAB- K_d values.

130

131 **Calibration and validation sets.** The triplicate spectra for each sample were imported into
132 Unscrambler[®] multivariate statistical analysis software version 9.8 (2008, CAMO Process ASA,
133 www.camo.com/products) and averaged. Soil properties (%SOC, soil pH, %sand, %silt and
134 %clay) and 2,4-D and atrazine K_d values were also imported. K_d values were predicted using
135 either NIRS spectra (see section: Use of NIRS to predict sorption) or pedotransfer functions (see
136 section: Pedotransfer functions). All calibrations used a test set method in which LAB- K_d values
137 were sorted from low to high values and divided into calibration (two-thirds of the total samples)
138 and validation (one-third of the total samples) sets by selecting every third sample for the
139 validation set. As indicated in Table S2 (Supplementary Information), for each site and herbicide

140 combination, the test set method resulted in approximately the same distribution of LAB- K_d
141 values in the calibration and validation sets.

142
143 Two different scenarios were tested to predict herbicide K_d values: 1) A site-specific approach in
144 which the calibration and validation sets were obtained from the same field (either Manitoba or
145 Saskatchewan), and 2) A regional approach in which the calibration sets of Manitoba and
146 Saskatchewan were combined to predict herbicide K_d values on the validation sets of Manitoba
147 alone, Saskatchewan alone, or Manitoba and Saskatchewan combined. This resulted in five
148 calibration/validation scenarios for each herbicide. The site-specific approach refers to a scenario
149 where a calibration model was developed for a site, and additional samples were collected in the
150 same soil-landscape to improve on the characterization of the spatial variability of herbicide
151 sorption in a simulation unit. The regional approach was included in order to explore the
152 feasibility of developing a generic NIRS model or pedotransfer function where data from
153 multiple sites are being combined to develop a model that could be used to improve on the
154 spatial resolution of pesticide sorption within and between simulation units at the same time.

155
156 **Use of NIRS to predict sorption.** Calibration development was done in Unscrambler[®] software
157 using protocols similar to those previously described (Dunn et al. 2002, Malley et al. 2004, Singh
158 et al. 2010, Singh et al. 2012) except that in this study the test set method allowed for validation
159 evaluation. The software allowed us to consecutively apply partial least squares regression
160 (PLS1 method in Unscrambler[®] software) to optimize the prediction of K_d values from spectral
161 data for the calibration set, the resulting optimized calibration equation within the software then
162 generated the prediction of K_d values from spectral data derived from the validation samples.

163 Trial calibrations consisted of performing mathematical pretreatments (using moving average
164 method) on the raw spectra by smoothing over 5, 11, 13, 21, or 41 wavelength points, and
165 transforming the spectra to the first or second derivative using derivative gaps of either 5, 11, 13,
166 21, or 41 wavelength points (Figure S2, Supplementary Information). Higher coefficients of
167 determinations (R^2), higher ratios of prediction to deviation (RPD), and lower standard error of
168 predictions (SEP) (Dunn et al. 2002, Malley et al. 2004) were generally achieved with a
169 mathematical pretreatment that used transformation of the spectra to the first derivative using 13
170 wavelength points left and right in Unscrambler[®] software. For the final calibrations, this
171 mathematical pretreatment was applied to each of the calibration/validation scenarios to estimate
172 2,4-D and atrazine K_d values in the validation samples. Throughout this paper, the predicted 2,4-
173 D and atrazine K_d values as applied to the soil horizons in the validation sets will be referred to
174 as NIRS- K_d values.

175

176 **Pedotransfer functions.** Using the same calibration and validation sets as for the NIRS method,
177 partial least squares regression (PLS1 method in Unscrambler[®] software) was applied to two-
178 thirds of calibration samples to establish pedotransfer functions using 2,4-D or atrazine LAB- K_d
179 values as the dependent (response) variable and soil properties (%SOC, soil pH, %sand, %silt
180 and/or %clay) as the independent variables. During calibration, independent variables that
181 contributed ≤ 0.1 to the coefficient of determination were sequentially removed, which
182 simplified the regression equations but maintained the same approximate prediction power. For
183 each of the calibration and validation scenarios, the best pedotransfer function was selected
184 based on the largest R^2 and the lowest SEP and bias values in the calibration model. Pedotransfer
185 functions were subsequently applied to the measured soil properties data of the validation

186 samples in order to calculate herbicide K_d values for the soil horizons in the validation set.
187 Throughout this paper, calculated 2,4-D and atrazine K_d values as applied to the soil horizons in
188 the validation sets will be referred to as SOIL- K_d values.

189
190 **PRZM simulations.** Each validation sample was set as a simulation unit with a 10 cm depth and
191 0.1 cm compartments (PRZM simulation layers). The herbicide mass leached (referred as L_m ,
192 kg/ha) below 10 cm depth was set as the output parameter to be tested. Each validation sample in
193 the ten calibration and validation scenarios had a measured LAB- K_d value, a predicted NIRS- K_d
194 and a calculated SOIL- K_d value. These LAB- K_d , NIRS- K_d , or SOIL- K_d values were used as
195 input parameters in PRZM to calculate the herbicide mass leached as LAB- L_m , NIRS- L_m and
196 SOIL- L_m , respectively. A total of 3,564 PRZM simulations were conducted. AutoPRZM
197 (McQueen et al. 2007) was used to automate the construction of the PRZM input file, the running
198 of PRZM, and the extraction of data from the PRZM output file.

199
200 PRZM (Carsel et al. 1998) is a one-dimensional pesticide fate model, currently being used in
201 regulatory and policy assessments for the large scale risk assessments in North America and
202 European Union. The PRZM manual is available on-line and explains the model in great detail
203 (<http://www.epa.gov/athens/publications/reports/Suarez600R05111PRZM3.pdf>). The
204 fundamental concept of PRMZ is that equations are used to calculate water distribution between
205 soil layers and to distribute a pesticide between the solid, water and gas phases while undergoing
206 transformation. K_d value is a sensitive parameter in the model as it is inversely related to the
207 amount of the pesticide moving with leachate (Farenhorst et al. 2009). Simulations were
208 performed using a 24-h time step for temperature and precipitation data. Temperature and

209 precipitation data were obtained from a meteorological station at the Brandon airport that is
210 located about 14 km from the Manitoba site. The same weather data were used for both
211 Manitoba and Saskatchewan sites to allow for a more direct comparison in PRZM simulation
212 outputs between sites.

213

214 Field capacity and wilting point are key variables describing vertical water flow and
215 evapotranspiration in the model. Field capacities and wilting points were calculated for each
216 horizon by applying measured %SOC, %sand, %clay, and bulk density to equations based on the
217 work of Rawls et al. (1982) and provided in the PRZM manual (Carsel et al. 1998). Potential
218 evapotranspiration was calculated using the method of Hargreaves and Samani (1985) using
219 REF-ET[®] given by Allen (2001). Soil profile drainage was set as well-drained for all horizons.
220 All simulations were started with soils at field capacity, but a warm-up time of one year was used
221 to provide for more realistic moisture conditions at the time of application of the herbicides in
222 year one. Preliminary PRZM simulations indicated that a longer warm-up time of up to five
223 years had no significant influence on modeling results. The herbicide application rates were 445
224 g/ha for 2,4-D and 1,073 g/ha for atrazine, which approximate the recommended rates. We
225 assumed that the herbicides were applied at the beginning of a growing season (May 3rd), and the
226 end of the simulation was set at November 31st, which is the average date when there is
227 permanent snow cover in the Prairie region where the field sites are located (Potter 1965).
228 Degradation was calculated in the model assuming first-order kinetics and using half-lives of 66
229 days for atrazine and 14 days for 2,4-D as obtained from the Pesticide Properties DataBase
230 (University of Hertfordshire 2013).

231

232 **Statistical evaluations of the success of the prediction methods used.** For each validation set,
233 coefficient of determination (R^2) was calculated between LAB- K_d vs. NIRS- K_d , and LAB- K_d vs.
234 SOIL- K_d , and LAB- L_m vs. NIRS- L_m , and LAB- L_m vs. SOIL- L_m . Linear regression plots were
235 also developed with NIRS- K_d , SOIL- K_d , NIRS- L_m or SOIL- L_m as independent variables and
236 LAB- K_d or LAB- L_m as dependent variables to determine regression equations along with the
237 root mean square error of prediction (RMSE). For each herbicide, calibration/validation
238 scenarios with larger R^2 and smaller RMSE values were deemed the more successful approaches
239 to estimating 2,4-D and atrazine K_d values for use in PRZM. For some samples in the validation
240 sets, a few predictions resulted in negative NIRS- K_d , and/or SOIL- K_d values. These soil horizons
241 were removed prior to the statistical evaluations.

242

243 **RESULTS AND DISCUSSION**

244

245 **NIRS and pedotransfer functions predictions.** The RPDs of NIRS validations ranged from
246 2.15 to 3.17 in the site-specific approach (Table 1). Dunn et al. (2002) suggests three categories
247 for RPD in soil analysis: poor, < 1.6 ; acceptable, $1.6-2.0$; and excellent, > 2.0 . In the regional
248 approach, NIRS validations also had $RPD > 2$ in all cases, except for atrazine in the
249 Saskatchewan validation data ($RPD = 1.26$) (Table 1). Atrazine and 2,4-D LAB- K_d values were
250 significantly positively associated with SOC in both Manitoba and Saskatchewan with
251 correlation coefficients (R) ranging from 0.89 to 0.94 (Singh et al. 2014). NIRS predictions for
252 SOC often yield RPD values > 2.0 (Malley et al. 2000, Chang and Laird 2002) and the feasibility
253 of using NIRS to predict herbicide sorption largely relies on the sorption of the herbicide being
254 highly significantly correlated to SOC. SOC and pH were represented in all pedotransfer

255 functions, both in the site-specific and in the regional approach (Table 2). Atrazine and 2,4-D
256 LAB- K_d values were significantly negatively associated with soil pH in both Manitoba and
257 Saskatchewan with correlation coefficients ranging from -0.30 to -0.63 (Singh et al. 2014). Other
258 researchers have reported that 2,4-D and atrazine sorption increases with increasing SOC and
259 decreasing soil pH (Novak et al. 1997, Rodriguez-Rubio et al. 2006, Hiller et al. 2008,
260 Villaverde et al. 2008, Prado et al. 2014).

261
262 2,4-D LAB- K_d ranged from 0.03 to 6.78 L/kg in Manitoba and from 0.01 to 3.88 L/kg in
263 Saskatchewan (Table S2, Supplementary Information) and the medians of the 2,4-D LAB- K_d
264 data at the two sites were not significantly different (Mann-Whitney test, $P = 0.92$). For 2,4-D,
265 the mean K_{oc} value (sorption coefficient normalized by soil organic carbon content) was 56 L/kg
266 for Manitoba and 170 L/kg for Saskatchewan, where NIRS (57 L/kg for Manitoba and 181 L/kg
267 for Saskatchewan) and the pedotransfer functions (57 L/kg for Manitoba and 146 L/kg for
268 Saskatchewan) also produced a similar mean K_{oc} . These K_{oc} values were in agreement with the
269 literature 2,4-D K_{oc} range of 31-275 L/kg (University of Hertfordshire 2013). The soil horizons
270 in the validation sets showed strong agreement between measured and predicted 2,4-D K_d values
271 (Figure 1), ranging from $R^2 = 0.83$ to 0.90 in the site-specific approach (Table 3) and from $R^2 =$
272 0.82 to 0.90 regional approach (Table S3, Supplementary Information). For 2,4-D, agreement
273 between LAB- L_m and either NIRS- L_m or SOIL- L_m ranged from $R^2 = 0.57$ to 0.78 in the site-
274 specific approach (Table 3) and from $R^2 = 0.52$ to 0.78 in the regional approach (Table S3,
275 Supplementary Information). Agreement were always weaker for L_m than K_d because, like other
276 pesticide fate models (Dubus et al. 2003a), PRZM is very sensitive to K_d values, so small

277 differences between measured and predicted K_d values lead to proportionally larger differences
278 in the herbicide mass leached (Farenhorst et al. 2009).

279
280 Atrazine LAB- K_d values ranged from 0.08 to 8.71 L/kg in Saskatchewan but from 1.01 to 35.14
281 L/kg in Manitoba (Table S2, Supplementary Information). For atrazine, the mean K_{oc} value was
282 333 L/kg for Manitoba and 267 L/kg for Saskatchewan, where NIRS (339 L/kg for Manitoba and
283 270 L/kg for Saskatchewan) and the pedotransfer functions (344 L/kg for Manitoba and 262 L/kg
284 for Saskatchewan) also produced a similar mean K_{oc} . The atrazine K_{oc} reported in the literature
285 ranges from 89 to 513 L/kg (University of Hertfordshire 2013). Under the pH conditions studied,
286 atrazine is primarily in non-ionic form, thus promoting hydrophobic interactions with organic
287 matter. As discussed in Singh et al. (2014), SOC increased significantly from A-horizons in
288 Manitoba > A-horizons in Saskatchewan > all other horizons. In Manitoba, Ap and Ah horizons
289 in depressions showed particularly large SOC and atrazine LAB- K_d values (> 20 L/kg) (Singh et
290 al. 2014). The medians of the atrazine LAB- K_d data at the two sites were significantly (Mann-
291 Whitney test, $P = <0.001$) different and the regional approach for atrazine was not successful,
292 with correlations between LAB- L_m and either NIRS- L_m or SOIL- L_m being $R^2 \leq 0.25$, regardless
293 of the validation scenario used.

294
295 For the site-specific analyses, the soil horizons in the validation sets showed strong ($R^2 \geq 0.79$)
296 agreement between measured and predicted atrazine K_d values for both Manitoba and
297 Saskatchewan (Table 3, Figure 2). For atrazine, the agreement between LAB- L_m and either
298 NIRS- L_m or SOIL- L_m were stronger for Saskatchewan than Manitoba (Table 3) because of the
299 relatively large SEP and bias observed for the models predicting atrazine K_d values in Manitoba

300 (Tables 1 and 2). In addition, for herbicides that have relatively long half-lives such as atrazine,
301 variations in sorption input parameters, in particular, can lead to differences in the predicted
302 herbicide mass leached when K_d values are large. For example, for a hypothetical soil horizon,
303 reducing the K_d value by 10% increased the mass of atrazine leached by a factor of 2.2 when
304 atrazine's K_d value was set to 3.75 L kg^{-1} (the median atrazine LAB- K_d in Manitoba, Table S2,
305 Supplementary Information), but by a factor of only 1.2 for a K_d of 1.11 L kg^{-1} (the median
306 atrazine LAB- K_d in Saskatchewan, Table S2, Supplementary Information).

307

308 **Integration of NIRS into pesticide fate modelling as part of large-scale assessments.** Soil
309 properties vary in fields or catchments because of intrinsic (e.g., irregularities in parent material
310 deposition) and extrinsic (e.g., tillage) factors (Lindstrom et al. 1992, Goderya 1998, Phillips
311 2001, Park and Vlek 2002, Li et al. 2007). Sorption processes respond to the heterogeneity of
312 soil properties that exists in fields or catchments, as shown in studies for pesticides 2,4-D,
313 atrazine, bentazone, glyphosate, imazethapyr, isoproturon, mecoprop, metamiltron, napropamide
314 and trifluralin (Elabd and Jury 1986, Novak et al. 1997, Oliveira et al. 1999, Coquet and Barriuso
315 2002, Rodriguez-Cruz et al. 2006, Farenhorst et al. 2008, Singh et al. 2014). The strength of the
316 current study is that it demonstrates that NIRS spectra can be used as a tool to rapidly measure
317 large numbers of samples for sorption parameters, and that such data can be integrated into
318 pesticide fate models. Relative to LAB- K_d values, the NIRS spectra and pedotransfer function
319 approaches were equally successful in characterizing the spatial variability of herbicide sorption
320 in soil-landscapes, and hence in predicting the mass of 2,4-D or atrazine in the soil horizons of
321 the validation data sets. An added benefit to NIRS is the non-destruction of samples and the
322 rapid nature of the analysis, leading to more rapid throughput of the many samples needed to

323 characterize spatial variability of herbicide sorption in field or catchments. Also, NIRS spectra
324 can be used to predict the values of a range of soil properties in soil-landscapes, including SOC
325 and soil pH (Malley et al. 2000, Martin et al. 2002, Singh et al. 2012).

326
327 Governments use pesticide fate models to evaluate the impact of agriculture on water resources,
328 and to augment national water monitoring programs in the regulatory practices of pesticide
329 environmental exposure assessments (Dubus et al. 2003a, Gagnon et al. 2014). There are several
330 ways by which NIRS can be integrated with these large-scale assessments. Regional approaches
331 to predicting K_d values from NIRS spectral data can be developed providing that the calibration
332 model is derived from a combined set of fields that each have similar statistical population
333 characteristics in K_d values. In its simplest form, NIRS can be used as a screening tool in which
334 K_d values in soil horizons are predicted from NIRS spectral data and used as input parameters in
335 pesticide fate models to calculate the herbicide mass leached in soil profiles. Regression
336 equations (examples in Tables 3 and S3, Supplementary Information) can be applied prior to the
337 pesticide fate simulations to adjust the predicted NIRS- K_d values to approximate LAB- K_d values,
338 or applied after the pesticide fate simulations to calculate the approximate herbicide mass
339 leached that would have been predicted when using LAB- K_d values as input parameters.

340
341 In stochastic risk assessments, probability density functions (PDFs) help account for spatial
342 variations in sorption input parameters (Berg et al. 2008, Heuvelink et al. 2010). This allows for
343 a deterministic pesticide fate model to be run repeatedly within a simulation unit, each time using
344 a different sorption input parameter derived from a statistical distribution that is represented by
345 the PDF. Model users typically assume a normal, log-normal, or uniform distribution to describe

346 variability in sorption parameters at the large scale (Nofziger et al. 1994, Dubus and Brown
347 2002, Warren-Hicks et al. 2002). However, because PDFs are typically developed using K_d data
348 obtained from a small number of soil profiles (Berg et al. 2008, Heuvelink et al. 2010), the
349 construction of PDFs is strongly influenced by subjective decisions made by the model user
350 (Dubus et al. 2002). For example, although presented with the same K_d data from 18 soils,
351 different modelers chose to use different statistical distributions (log-normal, normal, or
352 triangular)(Beulke et al. 2006), and this user-subjective decision towards sorption input
353 parameters can have a more significant impact on the model predictions than the type of
354 pesticide fate model used (Boesten 2000). Through the use of NIRS spectra, numerous K_d values
355 can be estimated in the simulation area of interest, which should lead to better decisions about
356 the type of distribution assigned to the sorption input data as well as which minimum and
357 maximum K_d values to use in truncating PDFs (Beulke et al. 2006). Improvements to sorption
358 input data will reduce uncertainties in risk assessments of pesticide transport in fields and regions
359 (Dubus et al. 2003b).

360

361 **CONCLUSION**

362 Pesticide K_d values are highly variable in soil-landscapes and this spatial variability is difficult to
363 delineate especially when risk assessments are to be conducted for large agricultural regions. In
364 combination with batch equilibrium techniques, NIRS is a quick, economical and efficient tool to
365 optimize estimates of spatially variable pesticide K_d values in agricultural fields. The results
366 showed that NIRS can be easily integrated with pesticide fate models to estimate input K_d values
367 for herbicides 2,4-D and atrazine and calculate the approximate herbicide mass leached. NIRS
368 calibrations were most successful for 2,4-D, which has a smaller K_d values and smaller half-life

369 than atrazine. Regional scale calibrations were also successfully developed for 2,4-D because the
370 K_d data sets from the fields in Manitoba and Saskatchewan had similar statistical distributions.
371 To reduce uncertainties in large-scale risk assessments of pesticide transport in fields and
372 regions, NIRS will be an appropriate tool for improving on sorption input data.

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Table 1. Accuracy of prediction for 2,4-D and atrazine NIRS- K_d values at Manitoba and Saskatchewan sites using a site-specific and regional approach to calibration.

Herbicide and Site		n*	R ²	SEP	Bias	RPD
Site-Specific Approach	2,4-D constituent					
	Manitoba validation	103	0.90	0.47	-1.00 x 10 ⁻²	3.17
	Saskatchewan validation	95	0.86	0.33	3.00 x 10 ⁻²	2.66
	Atrazine constituent					
	Manitoba validation	103	0.87	2.86	-1.80 x 10 ⁻¹	2.72
	Saskatchewan validation	95	0.79	0.94	-1.00 x 10 ⁻²	2.15
Regional Approach	2,4-D constituent					
	Manitoba validation	103	0.87	0.55	-4.00 x 10 ⁻²	2.77
	Saskatchewan validation	95	0.84	0.36	4.00 x 10 ⁻²	2.44
	Manitoba + Saskatchewan validation	198	0.86	0.47	4.19 x 10 ⁻⁵	2.70
	Atrazine constituent					
	Manitoba validation	103	0.90	2.73	-1.20 x 10 ⁻¹	2.86
	Saskatchewan validation	95	0.79	1.61	1.10 x 10 ⁻¹	1.26
Manitoba + Saskatchewan validation	198	0.87	2.35	-3.08 x 10 ⁻³	2.79	

*n = number of samples in the validations data set, R² = coefficient of determination, SEP standard error of prediction, Bias = mean difference between predicted and measured values, RPD = ratio of prediction to deviation. Reported R², SEP, Bias and RPD parameters are based on the evaluation of the validation data set (one-third of the total samples).

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Table 2. Calibration models developed using a site-specific and regional approach to calculate SOIL-K_d values for soil horizons in the validation sets at Manitoba and Saskatchewan sites.

Herbicide and Site		Calibration Model	R ² *	SEP	Bias
Site-Specific Approach	2,4-D constituent				
	Manitoba calibration	SOIL-K _d = 0.54 + 1.05*(SOC%) - 0.15*(pH)	0.90	0.48	2.00 x 10 ⁻²
	Saskatchewan calibration	SOIL-K _d = -0.54 + 0.89*(SOC%) + 0.08*(pH)	0.87	0.32	3.50 x 10 ⁻³
	Atrazine constituent				
	Manitoba calibration	SOIL-K _d = 4.32 + 5.21*(SOC%) - 0.78*(pH)	0.82	3.35	4.30 x 10 ⁻¹
	Saskatchewan calibration	SOIL-K _d = 0.04 + 1.90*(SOC%) + 0.03*(pH)	0.80	0.92	6.77 x 10 ⁻⁴
Regional Approach	2,4-D constituent				
	Manitoba calibration	SOIL-K _d = -1.69 + 0.98*(SOC%) + 0.16*(pH)	0.89	0.50	1.10 x 10 ⁻¹
	Saskatchewan calibration	same as above	0.81	0.38	-1.10 x 10 ⁻¹
	Manitoba + Saskatchewan calibration	same as above	0.87	0.47	3.00 x 10 ⁻³
	Atrazine constituent				
	Manitoba calibration	SOIL-K _d = 7.77 + 4.25*(SOC%) - 0.92*(pH)	0.79	3.90	2.80 x 10 ⁻¹
Saskatchewan calibration	same as above	0.60	2.25	1.80 x 10 ⁻¹	
Manitoba + Saskatchewan calibration	same as above	0.76	3.21	2.30 x 10 ⁻¹	

*R² = coefficient of determination, SEP standard error of prediction, Bias = mean difference between predicted and measured values. Reported R², SEP, and Bias parameters are based on the evaluation of the calibration data set (two-thirds of the total samples).

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Table 3. Regression equations showing the relation between predicted K_d values (NIRS- K_d or SOIL- K_d) and measured K_d values (LAB- K_d), and, for the calculated mass of herbicide leached, using the predicted K_d (NIRS- L_m or SOIL- L_m) and measured K_d (LAB- L_m) values as input parameters in the Pesticide Root Zone Model.

Herbicide and Site	Prediction Method	n*	Linear Regression Equation	RMSE	R ²
2,4-D constituent					
Manitoba	Near-infrared spectroscopy	90	LAB- $K_d = -4.04 \times 10^{-2} + 1.06 \times \text{NIRS-}K_d$	3.86×10^{-1}	0.85
Manitoba	Near-infrared spectroscopy	90	LAB- $L_m = 7.66 \times 10^{-3} + 0.89 \times \text{NIRS-}L_m$	6.37×10^{-4}	0.78
Saskatchewan	Near-infrared spectroscopy	94	LAB- $K_d = 9.79 \times 10^{-3} + 0.98 \times \text{NIRS-}K_d$	1.33×10^{-1}	0.83
Saskatchewan	Near-infrared spectroscopy	94	LAB- $L_m = 1.31 \times 10^{-2} + 0.80 \times \text{NIRS-}L_m$	8.07×10^{-4}	0.57
Manitoba	Pedotransfer function	90	LAB- $K_d = -7.74 \times 10^{-2} + 1.03 \times \text{SOIL-}K_d$	2.59×10^{-1}	0.90
Manitoba	Pedotransfer function	90	LAB- $L_m = 1.18 \times 10^{-2} + 0.79 \times \text{SOIL-}L_m$	7.37×10^{-4}	0.74
Saskatchewan	Pedotransfer function	94	LAB- $K_d = 6.68 \times 10^{-2} + 0.95 \times \text{SOIL-}K_d$	1.21×10^{-1}	0.85
Saskatchewan	Pedotransfer function	94	LAB- $L_m = 7.94 \times 10^{-3} + 0.83 \times \text{SOIL-}L_m$	6.48×10^{-4}	0.65
Atrazine constituent					
Manitoba	Near-infrared spectroscopy	98	LAB- $K_d = 2.68 \times 10^{-1} + 0.99 \times \text{NIRS-}K_d$	1.26×10^1	0.81
Manitoba	Near-infrared spectroscopy	98	LAB- $L_m = 1.70 \times 10^{-2} + 0.15 \times \text{NIRS-}L_m$	3.28×10^{-3}	0.27
Saskatchewan	Near-infrared spectroscopy	93	LAB- $K_d = 2.98 \times 10^{-2} + 0.98 \times \text{NIRS-}K_d$	8.99×10^{-1}	0.79
Saskatchewan	Near-infrared spectroscopy	93	LAB- $L_m = 6.27 \times 10^{-2} + 0.76 \times \text{NIRS-}L_m$	2.03×10^{-2}	0.63
Manitoba	Pedotransfer function	98	LAB- $K_d = -5.02 \times 10^{-1} + 1.03 \times \text{SOIL-}K_d$	1.22×10^1	0.81
Manitoba	Pedotransfer function	98	LAB- $L_m = 2.28 \times 10^{-2} + 0.21 \times \text{SOIL-}L_m$	3.47×10^{-3}	0.23
Saskatchewan	Pedotransfer function	93	LAB- $K_d = -1.18 \times 10^{-1} + 1.04 \times \text{SOIL-}K_d$	8.59×10^{-1}	0.80
Saskatchewan	Pedotransfer function	93	LAB- $L_m = 7.12 \times 10^{-2} + 0.85 \times \text{SOIL-}L_m$	2.29×10^{-2}	0.59

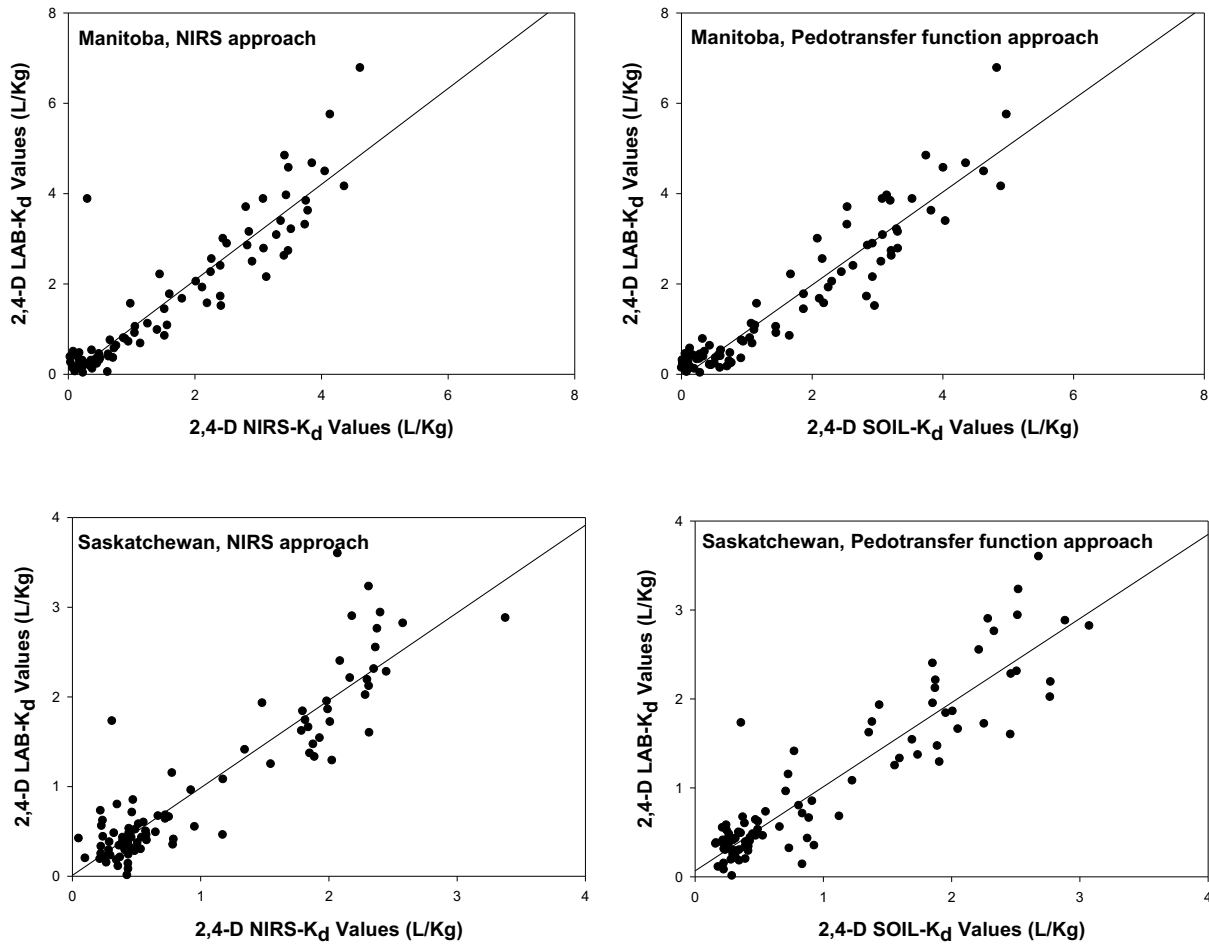
*n = number of samples in the validations data set, RMSE = root mean square error of regression, and R² = coefficient of determination. All regression equations are significant at p<0.001. Utilizing a site-specific approach to calibration, the reported RMSE and R² parameters are based on the evaluation of the validation data set (one-third of the total samples).

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632 **Figure 1.** Showing the relation between predicted K_d values (NIRS- K_d or SOIL- K_d) and
633 measured K_d values (LAB- K_d) at Manitoba and Saskatchewan soil-landscapes for the herbicide
634 2,4-D.

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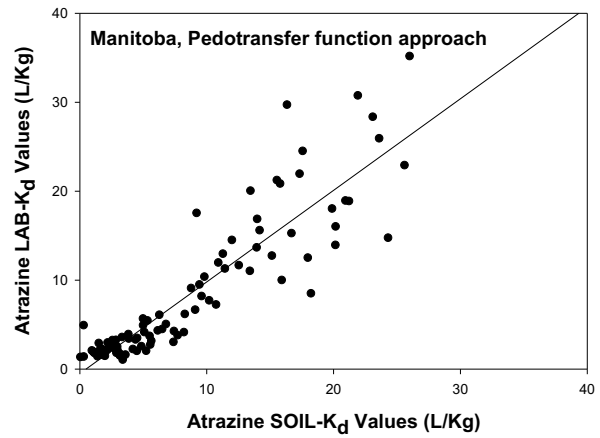
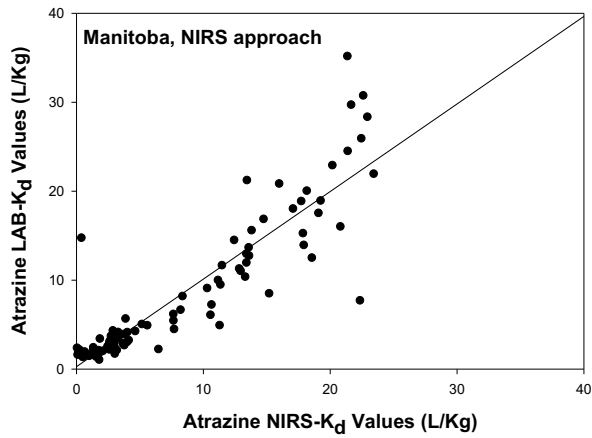
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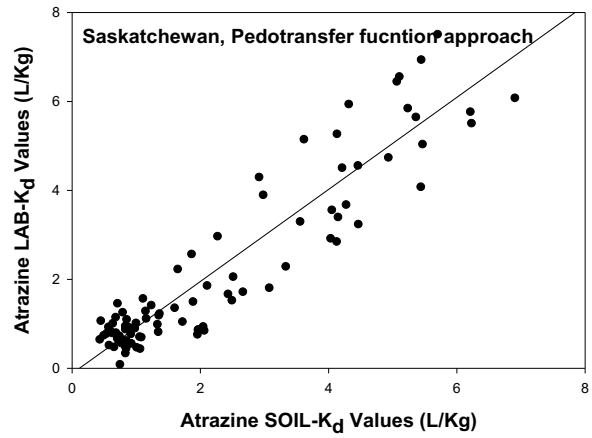
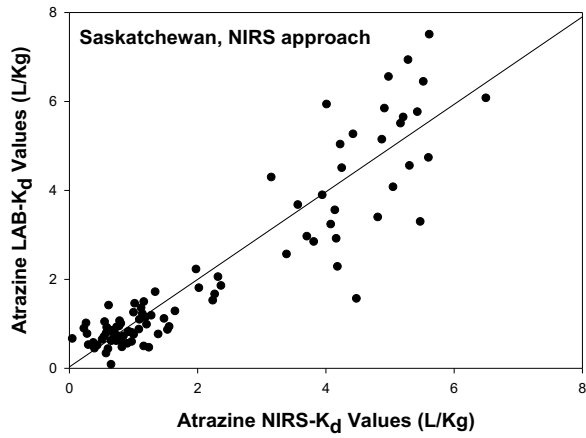
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643 **Figure 2.** Showing the relation between predicted K_d values (NIRS- K_d or SOIL- K_d) and
 644 measured K_d values (LAB- K_d) at Manitoba and Saskatchewan soil-landscapes for the herbicide
 645 atrazine.

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