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Predicting glyphosate sorption across New Zealand pastoral soils using basic soil properties or Vis–NIR spectroscopy

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ABSTRACT

Glyphosate [N-(phosphonomethyl) glycine] is the active ingredient in Roundup, which is the most used herbicide around the world. It is a non-selective herbicide with carboxyl, amino, and phosphonate functional groups, and it has a strong affinity to the soil mineral fraction. Sorption plays a major role for the fate and transport of glyphosate in the environment. The sorption coefficient (K_d) of glyphosate, and hence its mobility, varies greatly among different soil types. Determining K_d is laborious and requires the use of wet chemistry. In this study, we aimed to estimate K_d using basic soil properties, and visible near-infrared spectroscopy (vis–NIRS). The latter method is fast, requires no chemicals, and several soil properties can be estimated from the same spectrum. The data set included 68 topsoil samples collected across the South Island of New Zealand, with clay and organic carbon (OC) contents ranging from 0.001 to 0.520 kg kg⁻¹ and 0.021 to 0.217 kg kg⁻¹, respectively. The K_d was determined with batch equilibration sorption experiments and ranged from 13 to 3810 L kg⁻¹. The visible near-infrared spectra were obtained from 400 to 2500 nm. Multiple linear regression was used to correlate K_d to oxalate extractable aluminium and phosphorous and pH, which resulted in an R^2 of 0.89 and an RMSE of 259.59 L kg⁻¹. Further, interval partial least squares regression with ten-fold cross-validation was used to predict K_d by vis–NIRS, and an R^2 of 0.93 and an RMSECV of 207.58 L kg⁻¹ were obtained. Thus, these results show that both basic soil properties and vis–NIRS can predict the variation in K_d across these samples with high accuracy and hence, that glyphosate sorption to a soil can be determined with vis–NIRS.

1. Introduction

Glyphosate is a non-selective, broad-spectrum herbicide, which is intensively used for weed control worldwide (Borggaard and Gimsing, 2008). In fact, it is the most widely used herbicide in the world, and also in New Zealand, where it is used in about 90 different herbicides (Ministry for Primary Industries, 2015). The last survey of pesticide use in New Zealand was conducted in 2004: 344.3 t of the active ingredient were used which equals about 8% of the total pesticide use in 2004 (Manktelow et al., 2004). Glyphosate was the only pesticide determined in concentrations up to 950 ng g⁻¹ in sediment samples from estuarine sites located in residential areas of Auckland, New Zealand's biggest city (Stewart et al., 2014). However, in spite of its intensive use in agriculture and residential areas, the herbicide has not yet been included in the 4-yearly national survey of pesticide residues in

groundwater (Close and Skinner, 2012).

Glyphosate sorbs strongly to soil. Despite this, glyphosate and its metabolite aminomethylphosphonic acid (AMPA) have also been detected in ground and surface waters (Borggaard, 2011; Borggaard and Gimsing, 2008; Kjær et al., 2005; Norgaard et al., 2014). This may partly be explained by colloid-facilitated transport of glyphosate (de Jonge et al., 2004a; de Jonge et al., 2004b; Norgaard et al., 2013). The mobility of glyphosate in soil and hence the risk of leaching depend *inter alia* on sorption-desorption processes, biological and chemical degradation, and leaching through the soil matrix or macropores either in dissolved form or sorbed onto colloids (Al-Rajab et al., 2008; Arias-Estévez et al., 2008; Borggaard and Gimsing, 2008; de Jonge et al., 2000; Norgaard et al., 2014).

The sorption coefficient (K_d) is one of the most important soil properties for assessing the risk of pesticide leaching (Farenhorst et al.,

Abbreviations: Al_{ox}, oxalate extractable aluminium; AMPA, Aminomethylphosphonic acid; EC, electrical conductivity; Fe_{ox}, oxalate extractable iron; iPLSR, interval partial least squares regression; K_d , sorption coefficient; MLR, multiple linear regression; OC, organic carbon; OM, organic matter; P_{ox}, oxalate extractable phosphorous; PLSR, partial least squares regression; R^2 , coefficient of determination; RMSE, root mean square error; RMSEC, root mean square error of calibration, RMSECV, root mean square error of cross-validation; RPIQ, ratio of performance to interquartile range; SG, Savitzky-Golay; SNV, standard normal variate; VIF, variance inflation factor; vis–NIR, visible near-infrared; vis–NIRS, visible near-infrared spectroscopy

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2008). Glyphosate is composed of three functional groups (amino, phosphonate and carboxylate), and it sorbs strongly to the soil mineral fraction with high affinity for iron and aluminum oxides (Borggaard, 2011; de Jonge et al., 2001; Gerritse et al., 1996; Sheals et al., 2002) and clay minerals (Borggaard and Gimsing, 2008; Glass, 1987; Sprankle et al., 1975). The literature on the effect of soil organic matter (OM) on the K_d of glyphosate report contrasting results (Borggaard and Gimsing, 2008; Vereecken, 2005): It was reported that OM can increase K_d (Dollinger et al., 2015; Piccolo et al., 1996), have no effect, or decrease K_d (Gerritse et al., 1996; Paradelo et al., 2015). The content of phosphate can decrease glyphosate sorption, because phosphate and glyphosate compete for the same sorption sites (Borggaard, 2011; de Jonge and de Jonge, 1999; de Jonge et al., 2001; Gimsing and Borggaard, 2010), although it has also been suggested that glyphosate and phosphate sorption can be additive (Borggaard and Gimsing, 2008).

Besides soil composition, soil chemistry also affect the K_d of glyphosate. It is well documented that an increase in pH is accompanied by a decreasing K_d of glyphosate (de Jonge and de Jonge, 1999; Gimsing et al., 2004; Paradelo et al., 2015). Glyphosate becomes more negatively charged with increasing soil pH, which increases the electrostatic repulsion between the negatively charged glyphosate and the soil surface (Dollinger et al., 2015). Cation exchange capacity is another factor which increases K_d (Dollinger et al., 2015), whereas increasing electrical conductivity (EC) decreases K_d , which might be caused by cations in solution that forms a complex with glyphosate, and thereby reduces sorption to the soil (Paradelo et al., 2015).

The K_d of glyphosate can be measured by batch equilibrium sorption experiments, and several authors suggest to estimate K_d from pedotransfer-functions with a set of easily measurable soil properties as input parameters (Dollinger et al., 2015; Gimsing et al., 2004; Paradelo et al., 2015). Pedotransfer-functions have proven useful for determining K_d , but the optimal set of soil properties for K_d determination depends on the specific dataset used (Paradelo et al., 2016). Prioritization of the soil properties required for estimating K_d remains a complex task. Visible near-infrared spectroscopy (vis-NIRS) has also been used to predict sorption coefficients of pesticides (Bengtsson et al., 2007; Forouzangohar et al., 2009; Paradelo et al., 2016). It is a rapid and cost efficient alternative to conventional soil analysis. Multiple basic and functional soil properties can be predicted from one visible near-infrared (vis-NIR) spectrum (Ben-Dor and Banin, 1995; Chang et al., 2001; Hermansen et al., 2016; Hermansen et al., 2017; Katuwal et al., 2018a; Katuwal et al., 2018b; Knadel et al., 2016; Stenberg et al., 2010). Detailed information about the organic and inorganic soil composition is embedded in the vis-NIR spectra. This information originates from overtone and combination bands from fundamental vibrations of different functional groups (CO, CH, OH, NH, and metal-OH) in the mid-infrared range (Clark, 1999; Hunt, 1977). These spectral signatures enable the wide applicability of vis-NIRS to predict soil properties (Ben-Dor and Banin, 1995; Stenberg et al., 2010).

Only one previous study has documented successful vis-NIRS prediction of K_d of glyphosate across a Danish agricultural field (K_d from 162 to 536 L kg⁻¹) (Paradelo et al., 2016). Iron and aluminium oxides as well as clay minerals have been found to be some of the main controllers of the K_d of glyphosate (Borggaard and Gimsing, 2008; Dollinger et al., 2015). These are soil properties with direct spectral signatures within the vis-NIR spectral range (Ben-Dor, 2002). Thus, there is a potential that vis-NIRS can predict the K_d of glyphosate across soils with larger variability. In this study, we used soil samples from New Zealand collected across the entire South Island, thus representing a wide range of soil orders, parent materials and mineralogy. Our specific objectives were to:

- i. Determine the set of soil properties that best describe the variation in the K_d of glyphosate.
- ii. Examine if the K_d of glyphosate can be predicted based on vis-NIRS spectra.

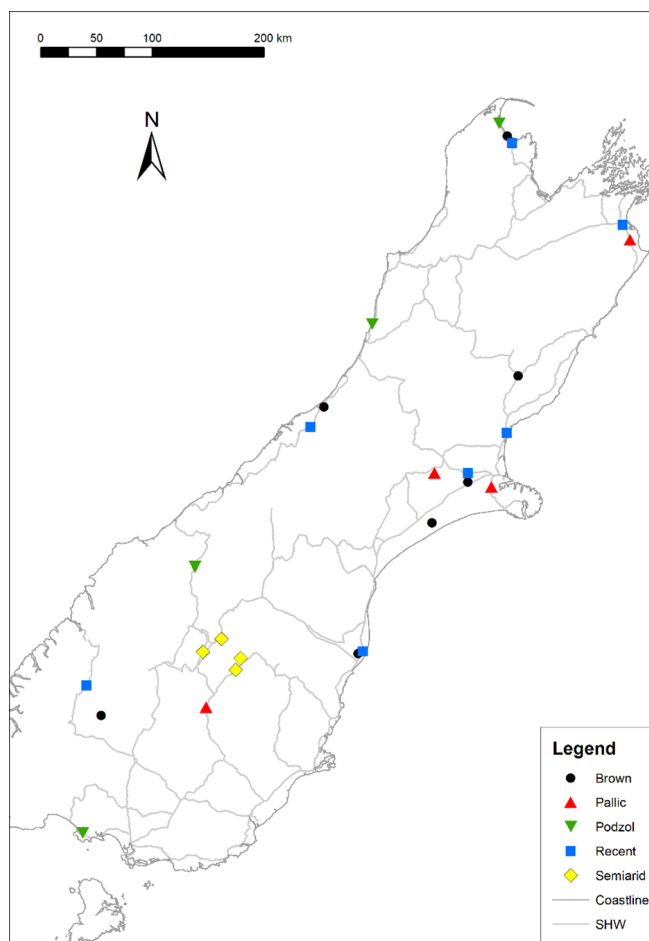


Fig. 1. Sampling sites at the South Island of New Zealand for the 68 soil samples included in this study. The twenty-six sampling sites represented five soil orders. SHW, state highway networks.

2. Materials and methods

2.1. Soil samples and soil properties

Soil samples were collected across New Zealand's South Island in summer 2012 (Hermansen et al., 2019). The 26 sampling sites were selected to represent the dominant soil orders under pasture in the island, being Brown, Pallic, Podzol and Recent soils (Hewitt, 2010). The soil order Semiarid was also included because it is the dominant soil order in one region (Fig. 1). In the classification of the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006) these soil orders correspond to Cambisols, Luvisols, Podzols, Fluvisols and Arenosols, respectively. At each site, three bulk soil samples (0–5-cm depth) were taken along a transect of 30 m length. The soil samples were sieved to < 2 mm, air-dried, and analyzed for texture on a Malvern laser sizer (Mastersizer 2000, Malvern Instruments, Malvern, UK) and organic carbon (OC) content using a Leco Truspec instrument (Blakemore et al., 1987). The pH was measured in 1 M KCl following the methodology of Blakemore et al. (1987) and EC was measured in a soil/water extract of 1:9 by volume. Oxalate extractable iron (Fe_{ox}), aluminium (Al_{ox}) and phosphorous (P_{ox}) were measured following the method of Schoumans (2000), and Olsen P was measured following the method of Olsen (1954).

2.2. Determination of glyphosate sorption coefficient

For the determination of the K_d of glyphosate, ¹⁴C labelled

glyphosate ([glycine 2-¹⁴C] glyphosate, N-(phosphonomethyl)glycine) was purchased from Perkin Elmer (Boston, USA). The ¹⁴C labelled glyphosate was dissolved in 0.01 M CaCl₂ to prepare stock solutions with an initial glyphosate concentration of 0.23 mg L⁻¹. To prevent microbial degradation, sodium azide (1.00 g L⁻¹) was added to the glyphosate solution (Soares et al., 2013).

The K_d of glyphosate was measured with batch sorption experiments in triplicate. Soil aliquots of 0.5 g were transferred to glass centrifuge tubes with Teflon caps and equilibrated with 0.5 mL of 0.01 M CaCl₂ for 24 h. Nine milliliters of glyphosate stock solution (0.23 mg L⁻¹) were added, after which the samples were rotated end-over-end at 30 rpm at 20 °C for 24 h. Then, the samples were centrifuged at 5000 rpm for one hour. From each sample, three mL of the supernatant were mixed with 17 mL scintillation cocktail (Packard Ultima Gold). A liquid scintillation analyzer (Packard Tri-carb 2250CA, Packard Instrument Co., IL) was used to measure the activity of the solution (DPM) which was then transformed to concentration (g L⁻¹). The specific amount of glyphosate sorbed (C_s; g kg⁻¹) was calculated from the soil dry weight (m_s) and the difference between the solution concentration (g L⁻¹) at apparent equilibrium (C_e) (i.e., after the 24-h incubation period) and the solution concentration (g L⁻¹) in equivalent samples from assays run without soil (C_i):

$$C_s = V(C_i - C_e)/m_s \quad (1)$$

where V is the volume in liters. The sorption coefficient of glyphosate, K_d (L kg⁻¹) was calculated from:

$$K_d = \frac{C_s}{C_e} \quad (2)$$

2.3. Multiple linear regression analysis

A forward multiple linear regression (MLR) analysis was performed to find a subset among the measured basic soil properties (clay, silt, sand, OC, pH, EC, Al_{ox}, Fe_{ox}, P_{ox}, and Olsen P) that would control the variation in the K_d of glyphosate across the 68 samples. In the MLR, it was a prerequisite that the effect of a given soil property was significant (p < 0.05) to be included. Further, the variance inflation factor (VIF) was used to indicate multicollinearity among the soil properties.

2.4. Vis-NIRS measurements

For this study, we used a NIRSTM DS2500 spectrometer (FOSS, Hillerød, Denmark). It measures diffuse reflectance in a sampling interval of 0.5 nm from 400 to 2500 nm (Hermansen et al., 2016). The instrument require approximately 30–50 g of air-dried and 2-mm sieved soil sample, which was transferred to a quartz sample cup with a cup diameter of 7 cm and a glass diameter of 6 cm. The cup was rotated inside the spectrometer, resulting in spectral measurements at seven positions. The seven scans were further averaged into one representative soil spectrum. The diffuse reflectance (R) was then converted into absorbance (A) (A = [log(1/R)]).

Table 1

Descriptive statistics of selected soil properties for New Zealand soil samples.

	Clay Kg kg ⁻¹	Silt Kg kg ⁻¹	OC ^a Kg kg ⁻¹	pH	EC ^b mS cm ⁻¹	Al _{ox} ^c mmol kg ⁻¹	Fe _{ox} ^c mmol kg ⁻¹	P _{ox} ^c mmol kg ⁻¹	Olsen P ^d mmol kg ⁻¹	K _d ^e L kg ⁻¹
Min	0.001	0.064	0.021	4.5	0.6	7.6	8.9	6.2	0.4	13.4
Max	0.520	0.896	0.217	6.3	10.0	340.0	260.0	68.0	7.1	3810.4
Mean	0.088	0.632	0.056	5.3	3.4	78.6	63.3	22.2	1.7	690.1

^a OC, Organic carbon.

^b EC, Electrical conductivity.

^c Al_{ox}, Fe_{ox} and P_{ox}, Oxalate-extractable aluminum, iron and phosphorous.

^d Olsen P, plant available phosphorous.

^e K_d, glyphosate sorption coefficient.

2.5. Multivariate data analysis

The Matlab program PLS Toolbox version 8.6.2 (Eigenvector Research Inc.) was used for multivariate data analysis. Partial least squares regression (PLSR) (SIMPLS algorithm; (de Jong, 1993) with ten-fold cross-validation was used to correlate the vis-NIR spectra to each of the soil properties to be predicted and thereby establish vis-NIRS prediction models. Different spectral preprocessing methods were applied to correct for nonlinear trends and additive and/or multiplicative effects in the spectrum, including Savitzky-Golay 1st and 2nd derivative (Savitzky and Golay, 1964), detrending, and standard normal variate (SNV) (Barnes et al., 1989). The regression coefficient from each model was used to indicate spectral bands important for predicting each soil property.

To further optimize the vis-NIRS model for pH, P_{ox}, Fe_{ox}, Al_{ox}, and the K_d of glyphosate, the variable selection method “interval partial least square regression” (iPLSR) (Hermansen et al., 2017; Knadel et al., 2018; Nørgaard et al., 2000; Zou et al., 2010) was applied on pretreated spectra to test whether these parameters could be predicted with higher accuracy using only a subset of spectral intervals compared to using the entire spectrum. Previous studies have shown that using spectral intervals found by forward iPLSR can decrease prediction errors and at the same time sort out irrelevant spectral information for a specific soil property, thereby decreasing model complexity (Hermansen et al., 2017; Knadel et al., 2018).

The root mean square error (RMSE) of calibration (RMSEC) and cross-validation (RMSECV), the coefficient of determination (R²), as well as the ratio of performance to interquartile range (RPIQ) were used as statistical measures to evaluate model accuracy. The RPIQ relates the RMSECV to the difference between the third (Q3) and first (Q1) quartile of the dataset (RPIQ = (Q3 - Q1)/RMSECV) (Bellon-Maurel et al., 2010).

3. Results and discussion

3.1. Soil properties and glyphosate sorption

This dataset represented five soil orders (Brown, Pallic, Podzol, Recent, and Semiarid) (Fig. 1) within the New Zealand soil classification scheme and thereby the soils covered a wide range in mineralogy and USDA texture classes (Table 1; Fig. 2). Eight soil types were represented (sand, loamy sand, sandy loam, loam, silty loam, silt, silty clay loam, and silty clay), with clay contents between 0.001 and 0.520 kg kg⁻¹ and OC contents between 0.021 and 0.217 kg kg⁻¹ (Table 1). The K_d of glyphosate spanned a wide range from 13.4 to 3810.4 L kg⁻¹ (Table 1). In comparison, the study of Dollinger et al. (2015) represented soils from 23 studies conducted in Asia, Europe, and South and North America with a gradient in the K_d of glyphosate of 0.06 to 403.5 L kg⁻¹, and the study of Paradelo et al. (2015) included two Danish field sites with K_d of glyphosate between 161 and 667 L kg⁻¹.

The soil property with the highest correlation to the K_d of glyphosate was Fe_{ox}, ranging from 8.9 to 260.0 mmol kg⁻¹ (r = 0.91,

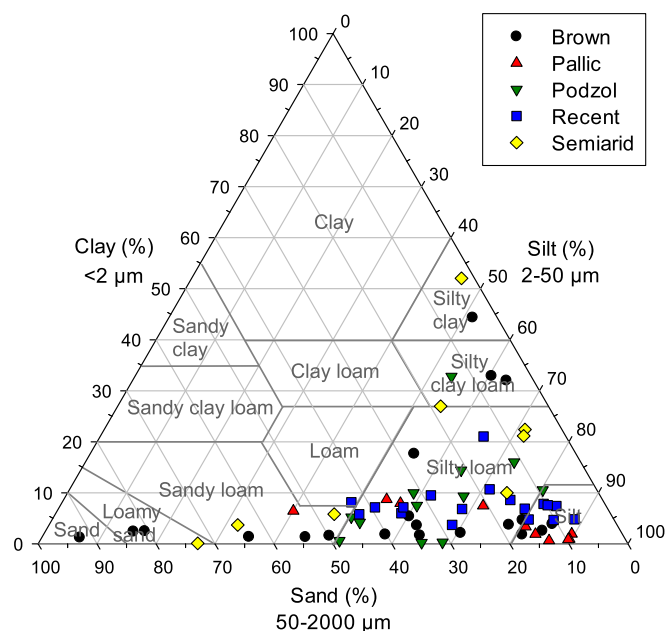


Fig. 2. Distribution of the soil samples from New Zealand ($n = 68$) within the USDA soil textural triangle.

$p < 0.001$) closely followed by Al_{ox} ranging from 7.6 to 340.0 $mmol\ kg^{-1}$ ($r = 0.89$, $p < 0.001$) (Table 2; Fig. 3c and d). This finding corroborates with the literature: The variable-charge surfaces of aluminum and iron oxides are known to be amongst the main sorbents for glyphosate in soil (Borggaard and Gimsing, 2008; Gimsing and Borggaard, 2010). The content of P_{ox} (6.2–68.0 $mmol\ kg^{-1}$) as well as pH (4.5–6.3) also contributed to explaining the variation in the K_d of glyphosate ($r = 0.37$, $p < 0.01$ and $r = -0.26$, $p < 0.05$, respectively) of these acidic soils (Table 2; Fig. 3a and b). Surprisingly, clay content did not correlate to the K_d of glyphosate (Table 2), although it has been found to be an important sorbent for glyphosate in other studies (Dollinger et al., 2015; Paradelo et al., 2015). This might be explained by the potentially wide variability in mineralogy amongst the soils of our dataset. Differences in glyphosate sorption capacity of clay minerals have been observed: Glass (1987) found montmorillonite to exhibit the highest capacity for glyphosate sorption followed by illite and then kaolinite, and Gimsing and Borggaard (2010) also found montmorillonite to sorb more glyphosate compared to illite.

Table 2

Pearson correlation matrix of selected soil properties for 68 soil samples collected across the South Island of New Zealand under pasture.

	Clay	Silt	Sand	OC ^a	pH	EC ^b	Al_{ox} ^c	Fe_{ox} ^c	P_{ox} ^c	Olsen P ^d	K_d ^e
Clay	1	-0.08	-0.44*** ^f	-0.04	-0.19	-0.18	-0.03	-0.02	-0.17	-0.17	0.05
Silt		1	-0.86***	-0.26*	-0.16	-0.36**	-0.24*	-0.09	-0.27*	-0.22	-0.09
Sand			1	0.26*	0.24	0.41***	0.23	0.1	0.33**	0.28*	0.06
OC				1	0.14	0.48***	0.3*	0.26*	0.27*	0.76***	0.18
pH					1	0.23	-0.02	-0.13	0.14	0.09	-0.26*
EC						1	0.41***	0.27*	0.49***	0.51***	0.21
Al_{ox}							1	0.91***	0.64***	-0.03	0.89***
Fe_{ox}								1	0.59***	-0.12	0.91***
P_{ox}									1	0.31**	0.37**
Olsen P										1	-0.19
K_d											1

^a OC; Organic carbon.

^b EC; Electrical conductivity.

^c Al_{ox} , Fe_{ox} and P_{ox} ; oxalate-extractable fractions of aluminum, iron and phosphorous.

^d Olsen P: Fraction of available phosphorous.

^e K_d ; glyphosate sorption coefficient.

^f Significance levels of *0.05, **0.01, and ***0.001.

3.2. Multiple linear regression analysis

The forward MLR revealed that the variation in the K_d of glyphosate could be explained using Fe_{ox} , Al_{ox} , P_{ox} and pH in combination. However, the intercorrelation between Al_{ox} and Fe_{ox} was high (VIF of 6.4 and 6.4, respectively) (Table 2), and therefore Fe_{ox} was excluded. Although Fe_{ox} was the single best predictor of the K_d of glyphosate, we obtained a slightly higher accuracy for the K_d of glyphosate in the MLR expression when including Al_{ox} ($R^2 = 0.89$, $RMSE = 259.59\ mmol\ kg^{-1}$) compared to including Fe_{ox} ($R^2 = 0.88$, $RMSE = 267.77\ mmol\ kg^{-1}$). The final MLR expression including Al_{ox} , P_{ox} , and pH is presented in Fig. 4.

Dollinger et al. (2015) suggested that cation exchange capacity and clay content could be applied to determine the K_d across soil samples from Europe, Asia, and North and South America (K_d from 0.83 to 318.82 $L\ kg^{-1}$). It was also suggested to estimate the amount of sorbed glyphosate from Fe and pH for a set of Danish soil samples (Gimsing et al., 2004). Further, clay, pH, P, and Al were found to be controlling the Freundlich sorption coefficients of soil samples from Argentina (De Gerónimo et al., 2018). Paradelo et al. (2015) found EC, clay and sand contents to be the best predictors of K_d across two Danish agricultural fields (K_d from 161 to 667 $L\ kg^{-1}$). However, the best subset of soil properties controlling K_d differed when the analysis was performed on each separate field. The best subset of soil properties controlling K_d included pH, clay, Fe, and Olsen P (K_d from 161 to 536 $L\ kg^{-1}$, clay: 0.06–0.14 $kg\ kg^{-1}$, OC: 0.02–0.08 $kg\ kg^{-1}$) for one field, and pH, clay, OC and Olsen P for the other field (K_d from 344 to 667 $L\ kg^{-1}$, clay: 0.14–0.19 $kg\ kg^{-1}$, OC: 0.02–0.02 $kg\ kg^{-1}$).

3.3. Qualitative analysis of vis-NIR spectra

It is possible to give a qualified suggestion for which soil properties are affecting the vis-NIR spectra, since several studies have reported which spectral bands are associated with absorption from different chemical bonds and electronic transitions of iron oxides (Clark et al., 1990; Post and Noble, 1993; Stenberg et al., 2010). However, it should be kept in mind that absorption from different organic and inorganic soil constituents is overlapping throughout the spectrum.

The vis-NIR spectra of the two samples exhibiting the highest (3810.35 $L\ kg^{-1}$; a Brown soil sample) and lowest K_d of glyphosate (13.44 $L\ kg^{-1}$; a Podzol soil sample) are depicted in Fig. 5. The sample with the highest K_d of glyphosate is also the sample with the highest content of Fe_{ox} (260 $mmol\ kg^{-1}$) and Al_{ox} (340 $mmol\ kg^{-1}$) in this dataset and it has a clay content of 0.016 $kg\ kg^{-1}$ and an OC content of 0.086 $kg\ kg^{-1}$. The sample with the lowest K_d of glyphosate has one of the lowest Fe_{ox} (12 $mmol\ kg^{-1}$) and Al_{ox} (14 $mmol\ kg^{-1}$) contents, a

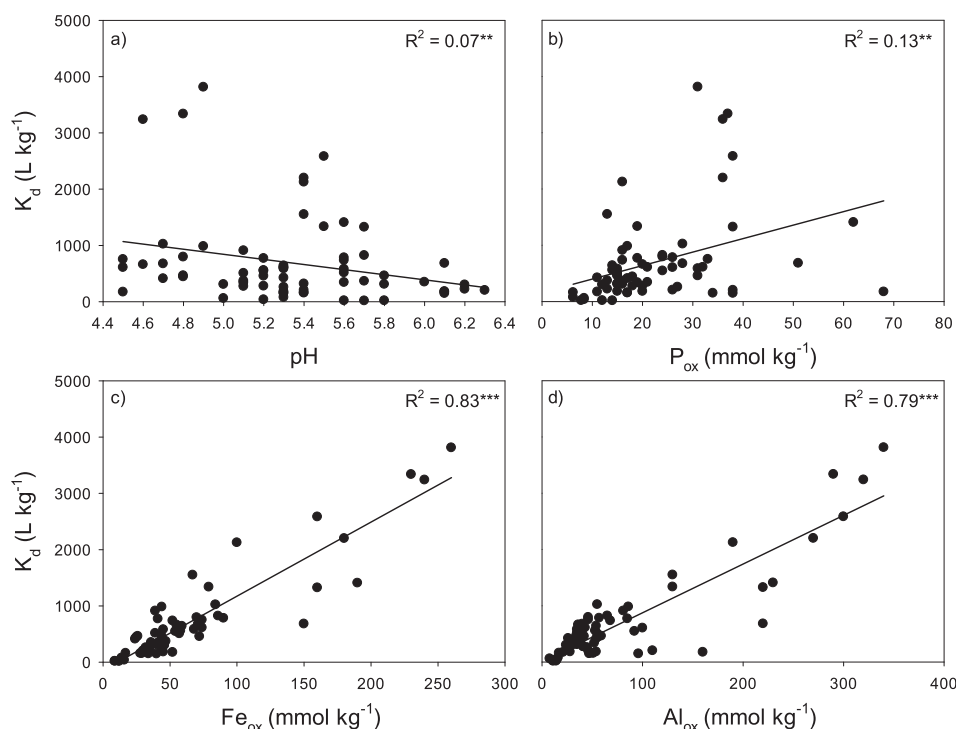


Fig. 3. The sorption coefficient of glyphosate (K_d) as a function of a) pH and oxalate-extractable b) phosphorous (P_{ox}), c) iron (Fe_{ox}) and d) aluminum (Al_{ox}). R^2 , coefficient of determination.

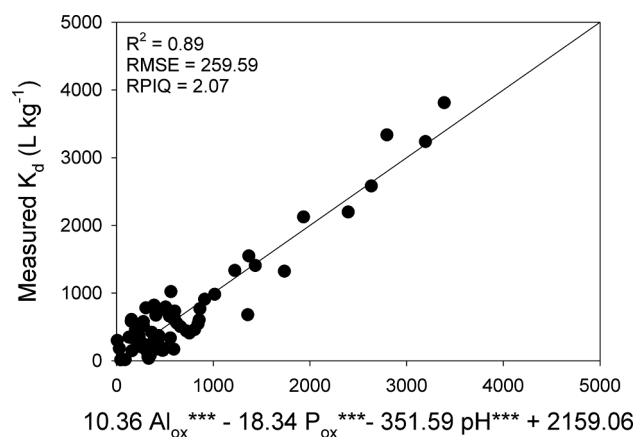


Fig. 4. Multiple linear regression analysis for the glyphosate sorption coefficient (K_d) including pH and oxalate-extractable aluminum and phosphorous. R^2 , coefficient of determination; RMSE, root mean square error; RPIQ, ratio of performance to interquartile range.

clay content of 0.075 kg kg⁻¹ and the highest OC content of 0.217 kg kg⁻¹. The difference in soil composition between these two samples is clear when comparing the spectra. The shape of the spectrum in the visible range was more concave for the soil with the highest K_d due to the high Fe_{ox} content, whereas the spectrum of the soil with lowest K_d was more convex due to the high OC content. A peak which could be caused by the presence of adsorbed and/or lattice OH around 1420 nm (Ben-Dor, 2002) and a peak which could be caused by adsorbed water around 1927 nm (Ben-Dor, 2002) were visible for both samples. The sample with the lowest K_d of glyphosate exhibited a local minimum in absorbance around 2222 nm. This absorption band is usually affected by the Al-OH bond (Knadel et al., 2013; Viscarra Rossel and Behrens, 2010).

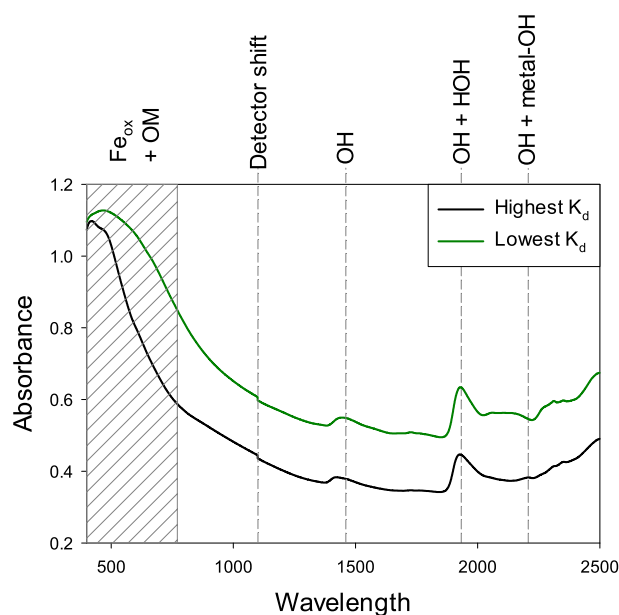


Fig. 5. Visible near-infrared absorbance spectra of the two samples in the dataset with the highest and lowest sorption coefficient of glyphosate (K_d). The highlighted region indicates a spectral region affected by overlapping signatures from iron oxides (Fe_{ox}) and organic matter (OM).

3.4. Interval partial least squares regression spectral intervals

With iPLSR, the optimal spectral pretreatment technique for pH prediction was 3rd order detrending followed by SNV, thereby reducing nonlinear trends and scattering effects from the spectrum. For P_{ox} , Fe_{ox} , Al_{ox} , and the K_d of glyphosate, the best results with iPLSR were obtained on spectra with no pretreatments applied (Tables 3 and 4 and Supplementary material, Table 1). A spectral subset including six intervals of adjacent wavelengths for the K_d of glyphosate vis-NIRS

Table 3

Spectral intervals from interval partial least squares regression (iPLSR) for pH, oxalate-extractable phosphorous (P_{ox}), iron (Fe_{ox}), and aluminium (Al_{ox}), and the sorption coefficient of glyphosate (K_d). For pH, spectral pretreatments included detrending (3rd order) followed by standard normal variate, whereas no pretreatment was applied for the remaining models.

Parameter	iPLSR intervals (nm)
pH	1000–1050 and 1900–2000
P_{ox}	580–700, 1000–1060, 1120–1180, 1420–1480, 1720–1780, 1900–1960, 2260–2320, and 2380–2440
Fe_{ox}	400–440, 480–520, 840–880, 1360–1400, 1680–1720, 1760–1800, 1880–1920, 2280–2320, and 2400–2480
Al_{ox}	550–600, 1000–1100, and 2100–2200
K_d	400–440, 560–600, 640–680, 1280–1320, 2160–2240, and 2280–2360

Table 4

Best performing models using interval partial least squares regression (iPLSR) for pH, oxalate extractable fractions of phosphorous (P_{ox}), iron (Fe_{ox}), and aluminum (Al_{ox}), and glyphosate sorption coefficients (K_d).

Parameter	Spectral pretreatment	Factors	RMSEC ^a	R ² (C) ^b	RMSECV ^c	R ² (CV) ^d	RPIQ ^e
pH	Detrending + SNV ^f	7	0.62	0.28	0.32	0.50	1.58
P_{ox}	None	15	3.58	0.91	4.86	0.84	2.67
Fe_{ox}	None	14	9.83	0.97	14.31	0.93	2.48
Al_{ox}	None	13	15.22	0.96	20.70	0.94	2.43
K_d	None	14	139.78	0.97	207.58	0.93	2.59

^a Root mean square error of calibration.

^b Regression coefficient from calibration.

^c Root mean square error of cross-validation.

^d Regression coefficient from cross-validation.

^e Ratio of performance to interquartile range.

^f Standard normal variate.

prediction was selected and included intervals from 400 to 440 nm, 560 to 600 nm, 640 to 680 nm, 1280 to 1320 nm, 2160 to 2240 nm, and 2280 to 2360 nm (Table 3).

The first three iPLSR intervals from 400 to 440 nm, 560 to 600 nm, and 640 to 680 nm are located in spectral regions that are affected by iron oxides, such as goethite (e.g., around 420, 434, and 650 nm) and hematite (e.g., at 404, 529 and 650 nm) (Knadel et al., 2013; Stenberg et al., 2010; Viscarra Rossel and Behrens, 2010; Viscarra Rossel et al., 2006). Further, the iPLSR model for Fe_{ox} is utilizing a similar spectral interval from 400 to 440 nm, which emphasizes that this spectral interval contains useful information about iron oxides. The iPLSR interval from 640 to 680 nm used for predicting the K_d is overlapping spectral intervals used for predicting P_{ox} (580–700 nm) and Al_{ox} (550–600 nm), which might reflect the intercorrelation to iron oxides for these soil parameters (Table 2). The iPLSR interval from 1280 to 1320 nm is overlapping a spectral range affected by OH bonds associated with minerals (Hunt, 1977) and some species of OM. It seems more probable that the model is utilizing information from soil moisture than OM due to the low correlation between the K_d of glyphosate and OC (Table 2). However, some literature states that OM is affecting the K_d of glyphosate (Borggaard and Gimsing, 2008; Dollinger et al., 2015; Gerritse et al., 1996; Paradelo et al., 2015; Piccolo et al., 1996; Vereecken, 2005), and therefore the quality and quantity of OM might also be affecting this vis-NIRS model. The iPLSR interval from 2160 to 2240 nm is located in a spectral region with signatures from the OH stretch and metal-OH bend (Viscarra Rossel and Behrens, 2010), which corroborates with the fact that the iPLSR model for Al_{ox} utilizes an overlapping spectral interval from 2100 to 2200 nm. The last spectral interval from 2280 to 2360 nm is located in a spectral region affected by different clay minerals and species of organic matter (Viscarra Rossel and Behrens, 2010), and this region was also important for the Fe_{ox} prediction (iPLSR interval from 2280 to 2320 nm).

3.5. Vis-NIRS models

The pH, P_{ox} , Fe_{ox} , and Al_{ox} were vis-NIRS-predicted to test whether vis-NIRS could predict basic soil properties controlling the K_d of

glyphosate (Table 4; Fig. 6). Using spectral intervals selected with iPLSR improved all four models as compared to using the entire spectrum (Supplementary material, Table 1).

The pH was estimated with moderate accuracy in cross-validation (R^2 of 0.50, RMSECV of 0.32, RPIQ = 1.58; Fig. 6a). Since pH is not spectrally active the ability of vis-NIRS to estimate pH might be caused by intercorrelations of pH with OC and clay contents (Wetterlind and Stenberg, 2010). Thus, the low accuracy for pH determination might be caused by the fact that pH possess a very low correlation to OC and clay contents (Table 2). The P_{ox} content was predicted with an R^2 of 0.84, an RMSECV of 4.86 mmol kg⁻¹, and an RPIQ value of 2.67 (Fig. 6b). Another study predicted P_{ox} with a R^2 of 0.79 and an RMSEP of 4.81 mmol L⁻¹ (P_{ox} range from 0.99 to 39.55 mmol L⁻¹) (Kawamura et al., 2019). Since phosphorous does not carry any direct spectral signatures, the vis-NIRS-prediction of P_{ox} is possible because it correlates to soil components that are spectrally active (Stenberg et al., 2010), as for example Fe_{ox} and Al_{ox} for this dataset (Table 2). The Fe_{ox} content was predicted well (R^2 of 0.93, RMSECV of 14.31 mmol kg⁻¹, RPIQ of 2.48; Fig. 6c). This accuracy is higher as compared with the study of Xu et al. (2018), in which Fe_{ox} was predicted with an R^2 of 0.85 and an RMSEP of 17.27 mmol kg⁻¹ (Fe_{ox} range from 1.61 to 222.58 mmol L⁻¹). The Al_{ox} prediction was also successful (R^2 of 0.94, RMSECV of 20.70 mmol kg⁻¹, RPIQ of 2.43; Fig. 6d), with a similar RPIQ as was obtained for the Fe_{ox} prediction. Compared to Paradelo et al. (2016) where Al_{ox} was predicted with an R^2 of 0.88 and an RMSECV of 4.85 mmol kg⁻¹ the R^2 was higher in this study, but the RMSECV was much lower in Paradelo et al. (2016), possibly due to a higher variability in our samples.

As Supplementary information, we successfully predicted OC content (R^2 of 0.64, RMSECV of 0.018 kg kg⁻¹), EC (R^2 of 0.74, RMSECV of 1.15 mS cm⁻¹), and Olsen P (R^2 of 0.64, RMSECV of 21.34 mmol kg⁻¹) using the entire spectrum. However, the soil texture could not be predicted, possibly due to the high variability in mineralogy of this dataset.

The K_d of glyphosate was successfully predicted, resulting in an R^2 of 0.93, an RMSECV of 207.58, and an RPIQ of 2.59 (Fig. 7; Table 4). Using iPLSR improved the model accuracy for both pH, P_{ox} , Fe_{ox} , Al_{ox} and the K_d of glyphosate as compared to using the entire spectrum.

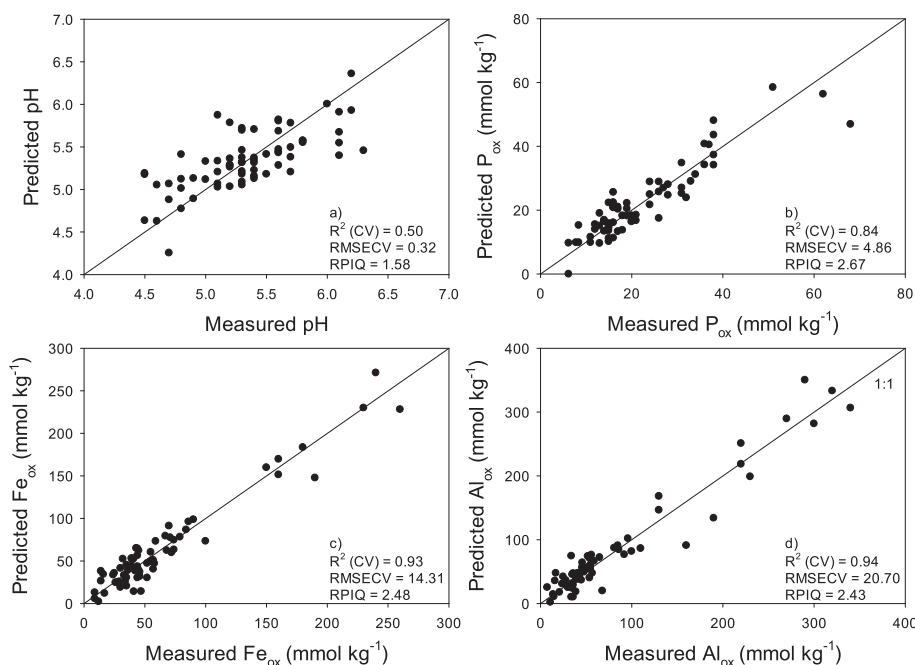


Fig. 6. Visible near-infrared spectroscopy predictions of a) pH and oxalate-extractable fractions of b) phosphorous (P_{ox}), c) iron (Fe_{ox}), and d) aluminum (Al_{ox}) using interval partial least squares regression. R^2 , coefficient of determination; RMSECV, root mean square error of cross-validation; RPIQ, ratio of performance to interquartile range.

Compared to Paradelo et al. (2016) who obtained an R^2 of 0.79 and an RMSECV of 45.54 L kg^{-1} using the full spectrum, we generated a higher R^2 and a higher error due to the large range in K_d of glyphosate present in our dataset.

4. Conclusion

This study included soil samples from New Zealand, covering a wide range of several soil properties. The key drivers for the variation in glyphosate sorption coefficient (K_d) included pH, and oxalate-extractable fractions of phosphorous (P_{ox}), iron (Fe_{ox}) and aluminum (Al_{ox}). Further, the best subset for a multiple linear regression for the K_d of glyphosate consisted of Al_{ox} , P_{ox} and pH.

We successfully established vis-NIRS prediction models for the soil properties controlling K_d of glyphosate. Based on RPIQ values, the P_{ox} vis-NIRS-model obtained the highest accuracy (RPIQ of 2.67) followed by the models for Fe_{ox} (RPIQ of 2.48), Al_{ox} (RPIQ of 2.43) and pH (RPIQ of 1.58).

The K_d of glyphosate was best and successfully predicted with a

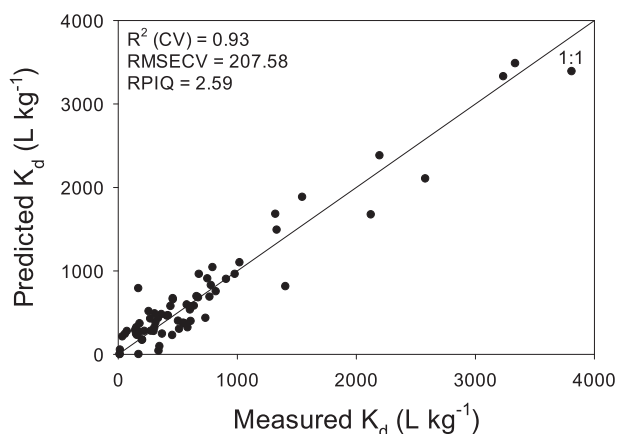


Fig. 7. Visible near-infrared spectroscopy predictions of the glyphosate sorption coefficient (K_d) using spectral intervals determined using interval partial least squares regression (iPLSR). R^2 , coefficient of determination; RMSECV, root mean square error of cross-validation; RPIQ, ratio of performance to interquartile range.

subset of the spectrum, found by interval partial least squares regression (iPLSR) including information from iron oxides, organic matter species, soil moisture, and aluminum oxides.

Based on the findings of this study and considering our dataset, it was more accurate to apply vis-NIRS to predict K_d of glyphosate than MLR analysis utilizing basic soil properties. Our study documents that the K_d of glyphosate can be vis-NIRS-predicted at large scale and not only at field-scale. The applicability of vis-NIRS for the prediction of K_d of glyphosate adds a functional soil property to the list of numerous basic and functional soil properties that can be obtained from a single vis-NIR spectrum.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2019.114009>.

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