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

Hermansen, Cecilie; Norgaard, Trine; Wollesen de Jonge, Lis; Moldrup, Per; Müller, Karin; Knadel, Maria
Published in:
Geoderma

DOI (link to publication from Publisher):
10.1016/j.geoderma.2019.114009

Creative Commons License
CC BY 4.0

Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

Link to publication from Aalborg University

Citation for published version (APA):
Hermansen, C., Norgaard, T., Wollesen de Jonge, L., Moldrup, P., Müller, K., & Knadel, M. (2020). Predicting glyphosate sorption across New Zealand pastoral soils using basic soil properties or Vis–NIR spectroscopy. Geoderma, 360(15 February 2020), [114009]. https://doi.org/10.1016/j.geoderma.2019.114009
Predicting glyphosate sorption across New Zealand pastoral soils using basic soil properties or Vis–NIR spectroscopy

Cecilie Hermansen⁎, Trine Norgaard⁎, Lis Wollesen de Jonge⁎, Per Moldrup, Karin Müller, Maria Knadela
Dept. of Agroecology, Faculty of Sciences and Technology, Aarhus University, Blichers Allé 20, P.O. Box 50, DK-8830 Tjele, Denmark
Dept. of Civil Engineering, Aalborg University, Thomas Manns Vej 23, DK-9200 Aalborg, Denmark
The New Zealand Institute for Plant & Food Research Limited (PFR), Land Use Impacts, Hamilton, New Zealand

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 (Kd) of glyphosate, and hence its mobility, varies greatly among different soil types. Determining Kd is laborious and requires the use of wet chemistry. In this study, we aimed to estimate Kd 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 dataset 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 Kd 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 Kd to oxalate extractable aluminium and phosphorous and pH, which resulted in an R² 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 Kd by vis–NIRS, and an R² 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 Kd 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 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 (Kd) is one of the most important soil properties for assessing the risk of pesticide leaching (Farenhorst et al.,

Abbreviations: Alox, oxalate extractable aluminium; AMPA, Aminomethylphosphonic acid; EC, electrical conductivity; Feox, oxalate extractable iron; iPLSR, interval partial least squares regression; Kd, sorption coefficient; MLR, multiple linear regression; OC, organic carbon; OM, organic matter; Pox, oxalate extractable phosphorous; PLSR, partial least squares regression; R², coefficient of determination; RMSE, root mean square error; 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

⁎ Corresponding author.
E-mail address: Cecilie.Hermansen@agro.au.dk (C. Hermansen).

https://doi.org/10.1016/j.geoderma.2019.114009
Received 25 July 2019; Received in revised form 24 September 2019; Accepted 12 October 2019
Available online 12 November 2019
0016-7061/ © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/BY/4.0/).
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 Kd of glyphosate report contrasting results (Borggaard and Gimsing, 2008; Vereecken, 2005). It was reported that OM can increase Kd (Dollinger et al., 2015; Piccolo et al., 1996), have no effect, or decrease Kd (Gerritse et al., 1996; Paradelo et al., 2015). The content of phosphate and carboxylate, and its orbs strongly to the soil mineral with high affinity for iron and aluminum oxides (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 affects the Kd of glyphosate. It is well documented that an increase in pH is accompanied by a decreasing Kd 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 Kd (Dollinger et al., 2015), whereas increasing electrical conductivity (EC) decreases Kd, 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 Kd of glyphosate can be measured by batch equilibrium sorption experiments, and several authors suggest to estimate Kd 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 Kd, but the optimal set of soil properties for Kd determination depends on the specific dataset used (Paradelo et al., 2016). Prioritization of the soil properties required for estimating Kd 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 Kd of glyphosate across a Danish agricultural field (Kd 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 Kd of glyphosate (Borggaard and Gimsing, 2008; Dollinger et al., 2015). These are soil properties required for estimating Kd 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 Kd of glyphosate across a Danish agricultural field (Kd 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 Kd of glyphosate (Borggaard and Gimsing, 2008; Dollinger et al., 2015). These are soil properties required for estimating Kd 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).

i. Determine the set of soil properties that best describe the variation in the Kd of glyphosate.

ii. Examine if the Kd of glyphosate can be predicted based on vis–NIRS spectra.
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 Kd 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 ºC 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 (Cs; g kg−1) was calculated from the soil dry weight (ms) and the difference between the solution concentration (gL−1) at apparent equilibrium (Ce) (i.e., after the 24-h incubation period) and the solution concentration (gL−1) in equivalent samples from assays run without soil (Ci):

$$C_s = \frac{V(C_0 - C_e)}{m_s}$$  \hspace{1cm} (1)

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

$$K_d = \frac{C_i}{C_s}$$  \hspace{1cm} (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, Alox, Feox, Pox, and Olsen P) that would control the variation in the Kd 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 NIRS™ 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 requires 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 to absorbance (A) (A = [log(1/R)]).

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; (deJong, 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 each soil property.

To further optimize the vis–NIRS model for pH, Pox, Feox, Allox, and the Kd of glyphosate, the variable selection method “interval partial least square regression” (iPLSR) (Hermansen et al., 2017; Knade 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, 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 Kd 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 Kd 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 Kd of glyphosate between 161 and 667 L kg−1.

The soil property with the highest correlation to the Kd of glyphosate was Feox, ranging from 8.9 to 260.0 mmol kg−1 (r = 0.91,
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 Kd 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 Kd 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.

### 3.2. Multiple linear regression analysis

The forward MLR revealed that the variation in the Kd 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 Kd of glyphosate, we obtained a slightly higher accuracy for the Kd 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 Kd across soil samples from Europe, Asia, and North and South America (Kd 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 Kd across two Danish agricultural fields (Kd from 161 to 667 L kg\(^{-1}\)). However, the best subset of soil properties controlling Kd differed when the analysis was performed on each separate field. The best subset of soil properties controlling Kd included pH, clay, Fe, and Olsen P (Kd 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 (Kd 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 Kd of glyphosate (13.44 L kg\(^{-1}\); a Podzol soil sample) are depicted in Fig. 5. The sample with the highest Kd 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 Kd of glyphosate has one of the lowest Fe_ox (12 mmol kg\(^{-1}\)) and Al_ox (14 mmol kg\(^{-1}\)) contents, a...
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 Feox 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).

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
The pH was estimated with moderate accuracy in cross-validation ($R^2 = 0.50$, 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 (Wetterlund 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 $Fe_{ox}$ prediction was also successful ($R^2$ of 0.94, RMSECV of 20.70 mmol kg$^{-1}$, RPIQ of 2.43; 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.

### Table 3
Spectral intervals from interval partial least squares regression (iPLSR) for pH, oxalate-extractable fractions of 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 aluminium ($Al_{ox}$), and glyphosate sorption coefficients ($K_d$).

| Parameter | Spectral iPLSR intervals (nm) | Factors | RMSEC$^a$ | $R^2$ (C)$^b$ | RMSECV$^c$ | $R^2$ (CV)$^d$ | RPIQ$^e$ |
|-----------|-------------------------------|---------|-----------|--------------|------------|--------------|----------|
| pH        | Spectral 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.  
$^g$ 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 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.

Acknowledgements

This study was funded by the European Union’s Horizon 2020 Research and Innovation Project ‘PROTINUS’ (grant number: 645717), France, which was counter-funded from the Royal Society of New Zealand. Further, funding was through the Aarhus University Research Foundation grant (grant number: AUFF-E-2016-9-36).

Appendix A. Supplementary data

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

References

Al-Rajab, A.J., Amellal, S., Schlavon, M., 2008. Sorption and leaching of $^{14}C$-glyphosate in agricultural soils. Agron. Sustainable Dev. 28, 419–428. https://doi.org/10.1051/ags/2008014.
Arias-Entérez, M., López-Periago, E., Martínez-Carballe, E., Simal-Gándara, J., Mejuto, J.C., García-Río, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. Agric. Ecosyst. Environ. 123 (4), 247–260. https://doi.org/10.1016/j.agee.2007.07.011.
Barnes, R.J., Bhano, M.S., Lister, S.J., 1989. Standard normal variate transformation and de-trending of near-infrared diffuse reflectance spectra. J. Appl. Spectrosc. 43 (5).
Bellon-Maurel, V., Fernandez-Alhamada, E., Palagos, B., Roger, J. M., McBratney, A., 2010. Critical review of chemometric indicators commonly used for assessing the quality of the prediction of soil attributes by NIRS spectroscopy. TrAC, Trends Anal. Chem. 29 (11), 1273–1281. https://doi.org/10.1016/j.trac.2010.06.005.

Ben-Dor, E., 2002. Near-infrared reflectance spectroscopy as a tool to predict pesticide sorption in soil. Bull. Environ. Contam. Toxicol. 75 (4), 364–372. https://doi.org/10.1007/s00128-002-0204-x.

Borggaard, O.K., 2011. Does phosphate affect soil sorption and degradation? – a review. TrAC, Trends Anal. Chem. 31 (1), 16–27.

Borggaard, O.K., Gimsing, A.L., 2008. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. Pest Manage. Sci. 64, 441–456. https://doi.org/10.1002/ps.1512.

Chang, C.W., Laid, D.A., Mausbach, M.J., Hurburgh, C.R., 2001. Near-infrared reflectance spectroscopy-principal components regression analysis of several soils. Soil Sci. Soc. Am. J. 65 (2), 480–490. https://doi.org/10.2136/sssaj2001.652640X.

Clark, R.N., 1999. Spectroscopy of rocks and minerals and principles of spectroscopy. In: Rencz, A.N. (Ed.), Remote Sensing for the Earth Sciences: Manual of Remote Sensing. John Wiley & Sons, Chichester, UK, pp. 3–58.

Clark, R.N., King, T.V.W., Klejwa, M., Szwazy, G.A., Vergo, N., 1990. High spectral resolution reflectance spectroscopy of minerals. Geoderma 59 (85), 12653–12680. https://doi.org/10.1016/0016-7061(90)90019-9.

Close, M.E., Skinner, A., 2012. Sixth national survey of pesticides in groundwater in New Zealand. Soil Sci. Soc. Am. J. 77 (2), 658–679. https://doi.org/10.2136/sssaj2012.0093.

De Geronimo, E., Aparicio, V.C., Costa, J.L., 2018. Glyphosate sorption to soils of Argentina. Estimation of affinity coefficient by petodractor function. Geoderma 322, 00288330.2012.707131.

Forouzangohar, M., Cozzolino, D., Kookana, R.S., Smernik, R.J., Forrester, S.T., 2016. Sorption of glyphosate and phosphate by contrasting Danish surfaces soils. Eur. J. Soil Sci. 67 (8), 1133–1143. https://doi.org/10.1111/ejss.12490.

Gimsing, A.L., Borggaard, O.K., 2010. Effect of phosphate on the adsorption of glyphosate in soils, clay minerals and oxides. Int. J. Environ. Anal. Chem. 82, 545–552. https://doi.org/10.1080/03067310500366574.

Glass, R.L., 1987. Adsorption of glyphosate by soils and clay minerals. J. Agric. Food Chem. 35 (7), 1073–1081. https://doi.org/10.1021/jf00146a018.

Hermansen, C., Kjaergaard, C., Moldrup, P., Greve, M.H., Gislum, R., de Jonge, L.W., 2016. Adsorption of glyphosate on goethite: molecular characterization of surface complexes. Environ. Sci. Technol. 50 (10), 4391–4400. https://doi.org/10.1021/acs.est.5b03944.

Hewitt, A.E., 2010. New Zealand Soil Classification. Landcare Research Science Series No. 1. Lincoln, third ed. Manaaki Whenua Press.

Hunt, G.R., 1977. Spectral signatures of particulate minerals in the visible and near-infrared. Geophysics 42 (3), 501–513. https://doi.org/10.1190/1.1440721.

I.W. Ministry for Primary Industries, 2015. Glyphosate – Overview of use and monitoring in New Zealand.

Nørgaard, L., Saudland, A., Wagner, J., Nielsen, J.P., Munck, L., Engelsen, S.B., 2000. Adsorption of glyphosate on goethite: molecular characterization of surface complexes. Environ. Sci. Technol. 34 (1), 271–283. https://doi.org/10.1021/es990887w.

Olsen, S.R., 1954. Estimation of Available Phosphorous in Soils by Extraction with Sodium Bicarbonate. U.S. Govt. Off. Washington.

Schoumans, O.F., 2000. Determination of the degree of phosphate saturation in non-calcareous soils. In: Pierzynski, G.M. (Ed.), Methodsof Phosphorus Analysis for Soils, Sediments, Residuals, and Waters. RaleighNC, USA, pp. 31–34.

Sheals, J., Sjöberg, S., Persson, P., 2002. Adsorption of glyphosate on goethite: molecular characterization of surface complexes. Environ. Sci. Technol. 36 (14), 3090–3095. https://doi.org/10.1021/es010295v.

Soares, A.A., Moldrup, P., Minh, L.N., Vendelboe, A.L., Schjonning, P., de Jonge, L.W., 2013. Sorption of phenanthrene on glass beads. Water Air Soil Pollut. 224 (4), 1519. https://doi.org/10.1007/s11270-013-1519-z.

Sprankle, P., Meggitt, W.F., Penner, D., 1975. Adsorption, mobility, and microbial degradation of glyphosate in the soil. Weed Sci. 23 (1), 4049–4055. https://doi.org/10.2136/wsc1975.03615995002300020014x.

Stewart, M., Olsen, G., Hickey, C.W., Ferreira, B., Jelić, A., Petrović, M., Barcelo, D., 2014. A survey of emerging contaminants in the estuarine receiving environment around New Zealand. Sci. Rep. 8. https://doi.org/10.1038/s41598-018-29306-9.

Stenberg, B., Viscarra Rossel, R.A., Mouazen, A.M., Wetterlind, J., 2010. Visible and near infrared spectroscopy in soil science. Adv. Agron. 107, 163–512. https://doi.org/10.1016/j.geoderma.2018.02.037.

Vice, E., 2015. Mobility and leaching of glyphosate: a review. Pest Manage. Sci. 71 (12), 1399–1411. https://doi.org/10.1002/ps.3682.

Wright, J., 2015. Visible-Near-Infrared Spectroscopy: A Practical Approach. Elsevier, Oxford, pp. 290–291.
Viscarra Rossel, R.A., Behrens, T., 2010. Using data mining to model and interpret soil diffuse reflectance spectra. Geoderma 158 (1–2), 46–54. https://doi.org/10.1016/j.geoderma.2009.12.025.

Viscarra Rossel, R.A., Walvoort, D.J.J., McBratney, A.B., Janik, L.J., Skjemstad, J.O., 2006. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. Geoderma 131 (1–2), 59–75. https://doi.org/10.1016/j.geoderma.2005.03.007.

Wetterlind, J., Stenberg, B., 2010. Near-infrared spectroscopy for within-field soil characterization: small local calibrations compared with national libraries spiked with local samples. Eur. J. Soil Sci. 61 (6), 823–843. https://doi.org/10.1111/j.1365-2389.2010.01283.x.

Xu, S., Zhao, Y., Wang, M., Shi, X., 2018. Quantification of different forms of iron from intact soil cores of paddy fields with vis-NIR spectroscopy. Soil Sci. Soc. Am. J. 82 (6), 1497–1511. https://doi.org/10.2136/sssaj2018.01.0014.

Zou, X., Zhao, J., Povey, M.J.W., Holmes, M., Mao, H., 2010. Variables selection methods in near-infrared spectroscopy. Anal. Chim. Acta 667 (1–2), 14–32. https://doi.org/10.1016/j.aca.2010.03.048.