Mid-infrared spectroscopy as an alternative to laboratory extraction for the determination of lime requirement in tillage soils

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ARTICLE INFO

ABSTRACT

Lime is a crucial soil conditioner to bring agricultural soils to optimum pH values for nutrient availability. Lime recommendations are typically determined in laboratory extractions, the most common being the "Shoemaker-McLean and Pratt" (SMP) buffer method, that requires carcinogenic reagents soon to be abolished under the EU legislation. As an alternative to wet chemistry, mid-infrared (MIR) spectroscopy has shown to be a cost-and time effective method at predicting soil properties. The capability and feasibility of diffuse reflectance infrared spectroscopy (DRIFTS) to predict lime requirement (LR) in tillage fields is examined. Samples from 41 cereal tillage fields (n = 655) are used to build a calibration for DRIFTS using partial least squares regression (PLSR). The samples were split into calibration set (31 fields, n = 495) and validation set (10 fields, n = 160). After pre-processing with trim, smoothing and standard normal variate, a calibration model using 6 latent variables, provided R^2 of 0.89 and root mean square error of cross-validation (RMSECV) of 1.56 t/ha. Prediction of all fields from the validation set resulted in R^2 of 0.76 and root mean square error of prediction (RMSEP) of 1.68 t/ha. The predictions of the single fields ranged from R^2 values of 0.41 to 0.72, RMSEP of 0.48 to 4.2 t/ha and ratios of performance to inter-quartile distance (RPIQ) of 0.45 to 3.56. It was shown that the signals of soil constituents having an influence on the LR were picked up in the spectra and were identified in the loading weights of the PLSR. While the error is too high to predict the variability of LR within the field, MIR prediction using field averages provided a viable alternative to current laboratory methods for blanket spreading of lime on tillage fields.

1. Introduction

One cornerstone for reaching sustainable soil utilization (FAO, 2009) is improved soil management. To achieve this, soil parameters have to be closely monitored, so that measures to improve soil quality can be put in place where and when needed (FAO, 2017; Karlen et al., 1997).

Lime is a crucial soil conditioner in both tillage and grassland systems. It helps to bring the soil pH ($-\log_{10} [H^+]$) to the optimum level for crop production. In humid climate, soils tend to acidify naturally due to the slight acidity of the rain in equilibrium with the atmospheric CO_2 (McLean, 1982). The acidic water percolates the soil and neutralizes with the basic cations in solution and transports these cations away from plant roots. In addition to the leaching of bases, at lower pH values (below pH 4.7 (Sparks, 2003)), aluminium (Al) adsorbed to clay minerals gets exchanged with the H^+ in the solution. Once the Al ion is

in solution, it is coordinated by H_2O molecules, which then, depending on the pH, hydrolyse and release H^+ ions. Below pH 4.7, Al^{3+} is the dominant species, which, in comparison to the $Al(OH)_2$ present until pH 6.5, is soluble and toxic to the plant root system (Sparks, 2003).

In productive agricultural systems the most important source of soil acidity is the application of chemical fertilizer based on ammonium N (Goulding, 2016). Added to soil, N-fertilizer is nitrified (Barak et al., 1997; Goulding, 2016), and if the resulting NO_3^- isn't taken up by the crops, it will get leached, causing acidification (Barak et al., 1997). The soil itself works as a buffer by exchanging the acid forming cations with basic cations which are adsorbed to the surface (clay minerals, organic matter). This buffering capacity is strongly dependant on the type and amount of clay minerals and organic matter (OM), as these factors govern the cation exchange capacity (CEC) (Thomas and Hargrove, 1984). Once this buffer system is exhausted, the pH drops rapidly with additional acidity introduced. With lower pH, nutrients such as P, K,

Mg, Ca and S will no longer be available for plant uptake. In addition, the availability of metals such as Fe, Mn, Cu, Zn, Co and Al also increases to toxic levels (Sparks, 2003; The Fertilizer Association of Ireland, 2016).

By applying lime ($CaCO_3$) to the soil, it neutralizes the acidity, and so helps to improve soil structure (and thus drainage), the solubility of nutrients and provides optimum growth conditions for soil microorganisms (Goulding, 2016). The general neutralization reaction of acidity with lime is shown in Eq. (1) (Goulding, 2016), which leads to an exchange of the adsorbed H^+ ions with the Ca^{2+} ions.

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \quad (1)$$
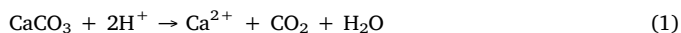
Or, taking the acidifying effect of Al^{3+} into consideration the overall reaction is described by Eq (2) (Sparks, 2003).

$$2Al\text{-soil} + 3CaCO_3 + 3H_2O \rightarrow 3 \text{ Ca-soil} + 2 Al(OH)_3 + 2CO_2 \quad (2)$$
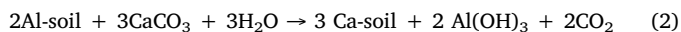
As soil acidification is influenced by numerous soil parameters, it is hard to measure with simple laboratory measurements and thus is typically summarized by the soil lime requirement (LR). The LR is expressed as the amount of lime needed to bring the soil to the target pH (in t/ha, usually measured in the top 10 cm of soil. It is a recommendation based on intrinsic soil properties such as CEC, clay mineralogy and OM which govern soil acidity (McLean, 1982). The strong dependence on these intrinsic soil parameters becomes apparent where soils with the same pH value can have different LR, largely because cation exchange mechanisms differ greatly among soil types. The exact LR is measured in time consuming incubation trials, where lime and soil are mixed and left to react and the resulting pH is measured. This test is not used routinely anymore, but is still used to calibrate laboratory methods (McLean, 1982). In commercial soil laboratories, routine methods are deployed that involve titration of the soil solution with a base (soil-base titration) or measuring the resulting pH after mixing the soil with a buffer (soil-buffer equilibration) (McLean, 1970). In the soil-buffer equilibration methods the soil is left to react with a solution made up from different buffers which in combination lead to linear change in pH with neutralized acidity (Sikora, 2006). Prominent buffer methods include the "Adams and Evans" buffer (Adams and Evans, 1962) the "Shoemaker, McLean and Pratt" buffer (SMP) (Shoemaker et al., 1961), the "Sikora" buffer, an alternative to the SMP buffer without hazardous chemicals (Sikora, 2006) and the "Mehlich" buffer which was developed for a soil pH range from 6.6 to 3.8 (Mehlich, 1976). Other methods include the LR determination by titration with calcium hydroxide ($Ca(OH)_2$) (Kissel et al., 2007) and texture and crop dependent models developed from long term trials in the United Kingdom (ROTH lime) (Goulding, 2016) Of the routine laboratory procedures, the "Shoemaker, McLean & Pratt" (SMP) buffer method delivers the most accurate results in the pH and LR ranges usually present in agricultural soils. However, SMP buffer solution contains hazardous substances such as potassium chromate (K_2CrO_4) and 4-nitrophenol, which are a threat to health and safety, making waste disposal an important financial factor. Potassium chromate is designated as a "Substance of Very High Concern" (SVHC) and included in the candidate list for authorization within the REACH framework (ECHA (European Chemicals Agency), 2010). As this compound will be phased out, there are several efforts to find an alternative method to determine the LR, with reliable results for agricultural soils (McLean et al., 1966; Tunney et al., 2010).

. Soil spectroscopy has emerged as a rapid, non-destructive method to analyse soils for a wide range of parameters, making it a potential alternative for the LR determination by lab extraction. Infrared (IR) spectra of soil samples contain information about the entire ensemble of soil components simultaneously. Using spectroscopy, the whole complex system causing soil acidity will be incorporated in the prediction of LR.

The main soil components which absorb IR radiation are OM (aliphatic, aromatic and amide vibrations), clay minerals (lattice water, O–H, Si-O and Al-O vibrations), sand (quartz, Si-O, lattice vibration), carbonates (X-H vibration) and Fe-oxides (Fe-O/H vibrations) (Janik et al., 1998; Nocita et al., 2015; Soriano-Disla et al., 2014; Stenberg and Viscarra Rossel, 2010; Vohland et al., 2014). Historically, two main regions in the IR are used for spectroscopy: near infrared (NIR, 700–2500 nm [14,000–4000 cm^{-1}]) and mid-infrared (MIR, 4000–400 cm^{-1} [2500 nm–25,000 nm]) (Sherman Hsu, 1997). These spectrally active components occur in variable combinations and concentrations in the analysed soil, depending on soil genetics, soil formation and land use interact with each other, creating a complex pattern of fundamental- overtone- and combination absorptions (see figure with raw spectra). While the NIR range is dominated by these broad overtone and combination patterns, the MIR range shows more fundamental absorptions and a clearer peak resolution (Hutengs et al., 2019). And while for some applications it is advantageous that the NIR range is insensitive to quartz, the MIR range is sensitive to quartz and other silicates, which gives it the possibility to also detect inorganic soil fractions (Reeves, 2010; Reeves et al., 2005). Initially, mostly NIR was used for soil spectroscopy, but with the emergence of more accessible Fourier Transform spectroscopy technology and diffuse reflectance scanning, the MIR range has moved into the focus of soil scientists and will be the method of choice in the present work (Janik et al., 1998; Soriano-Disla et al., 2014).

By means of "chemometric modelling" complex spectral patterns are analysed and key information in the spectra can be extracted. Chemometric modelling refers to multivariate models capable of dealing with a high number of variables, where, in the case of soil spectroscopy the whole spectrum is used to predict a soil parameter. The most intuitive and commonly used multivariate methods in soil spectroscopy are partial least squares regression (PLSR) and principal component regression (PCR). Here, the multivariate directions of maximum variance are determined for both the spectra ($\mathbf{X}$, predictor variables) and the laboratory data ($\mathbf{Y}$, response variables) and used to build a new "coordinate system". This coordinate system displays the whole dataset with an extremely reduced number of variables (from hundreds of wavelengths to < 10 factors (in PCR) or latent variables (LV, in PLSR)). The original data is displayed by scores (position of the samples in the new coordinate system) and loadings (influence of the variables (here: wavenumber) on the calculation of the scores). As a simplistic way of describing the following regression, one can say that those new "coordinate systems" are being rotated until the best fit is reached, which is then described by the regression equation (Esbensen and Swarbrick, 2018; Wold et al., 2001).

Another crucial part in chemometric modelling is the pre-treatment of the spectra. Hereby the goal is to get as much information from the spectra and decrease the influence of random noise and scattering.

Common pre-treatment measures are smoothing of the spectra, where several points of the spectrum are averaged to reduce the influence of random noise, using derivatives of the spectra (usually first or second derivative) to enhance the peaks (Savitzky and Golay, 1964), corrections for multiplicative effects on the spectra such as multiplicative scatter correction (MSC) (Geladi et al., 1985) and standard normal variate (SNV) (Barnes et al., 1989), normalization to make the different spectra comparable, and baseline corrections to compensate for an offset in the spectra due to differences during measurement. Trimming the spectra can also improve the information content of the spectra as regions of the spectrum which contain no viable information and only add to the noise can be cut out (Engel et al., 2013; O'Rourke et al., 2016; Rinnan et al., 2009). After successful pre-treatment, the model should have a small number of LVs (be parsimonious), maximize the variance explained by the model (R^2) and minimize the prediction error (root mean square error, RMSE) (Esbensen and Swarbrick, 2018).

Even if the LR isńt a soil parameter *per se* (there is no molecule indicating LR, much less a spectrally active one), it can still be predicted, as it is strongly dependent on the CEC and hence clay content,

clay type and OM (Chang et al., 2001; Janik et al., 1998; Soriano-Disla et al., 2014).

There are previously reported approaches in predicting the LR with IR spectroscopy. Tekin et al. (2013) developed an on-the-go NIR sensor, which was calibrated for pH. From the pH they developed a LR map according to DEFRA fertilizer manual (Department for Environment Food and Rural Affairs, 2010). Demattê et al. (2019) researched the precision of vis-NIR-SWIR spectroscopy (short wave IR) to predict LR based on CEC and base saturation (BS). They found high correlation between laboratory derived LR and spectral LR, proposing a hybrid approach with 20% of the samples analysed in the lab and the remaining 80% analysed spectrally. These approaches derived lime recommendations from proxy soil parameters, the only studies on LR derived from buffer pH were conducted by Viscarra Rossel et al.(2001) and Viscarra Rossel and McBratney (2001). They investigated the LR measured with a Mehlich-buffer response model measured at 122 points in a field in Australia. The MIR calibration resulted in an R^2 of 0.75 and a RMSE of 0.61 t/ha. Merry and Janik (1999) researched the potential of MIR to predict LR in different regions in Australia and could predict the LR on a large scale. A follow-up analysis of this report from 1999, or an indication of actual routine use of MIR for LR in Australia couldn't be found.

In Ireland, agronomic recommendations for LR are derived from the SMP buffer method which will shortly be discontinued due to the reagent composition including a SVHC. The objective of this study was to examine the application of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) in the MIR range in combination with chemometrics to predict LR and the feasibility of this approach to replace current wet chemical methods with spectral predictions. In productive agricultural systems LR is an agronomic recommendation given in tonne/ha and to our knowledge, no previous studies have predicted this recommendation using MIR calibrations derived from the SMP method directly. Therefore the objective of this study was to examine the ability of MIR to predict LR of cultivated soils and assess the viability of the predictions to substitute lengthy and hazardous laboratory extractions. The application of MIR models in precision agriculture was assessed by examining the predictive power of MIR to predict the variability of LR at field scale. This work focused on Irish tillage soils at multiple fields in regions where tillage is the predominant agricultural land use.

2. Materials and methods

2.1. Study sites/land use

A total of 655 soil samples were collected and analysed to build the calibration database from 41 tillage fields in the Republic of Ireland (Fig. 1). The fields were recently harvested, and the previous two crop rotations were cereals (wheat and barley). The field sizes ranged from 2 to 37 ha with a median size of 8 ha. In each field four zones based on field traffic patterns were sampled (headland, headland tramline, transition zone and main field), in replicate, resulting in 16 samples per field taken at a depth of 5–10 cm in the plough layer, accompanying bulk density samples at the same depth. This sampling pattern is part of a parallel study examining the spatial distribution of soil properties across trafficked and non-trafficked areas in fields.

3. Reference data acquisition

The disturbed samples were collected in cardboard sample boxes, brought to the laboratory and dried at 40 °C and mechanically sieved to 2 mm prior to analysis.

For pH analysis, 10 cm^3 of soil was mixed with 20 ml of deionized water and analysed with a pH autoanalyzer with Mettler Toledo "in lab Routine" pH electrode.

For the determination of LR, 20 ml of SMP buffer solution (pH 7.5,

T.E. Laboratories, Tullow, Ireland) was added to 10 cm^3 of dried and sieved (< 2 mm) soil and shaken for 30 min on a gyratory shaker at 180 rpm. The solution was filtered through a Whatman no. 2 filter and analysed for pH with a Mettler Toledo "InLab Routine" (Mettler Toledo, Columbus, Ohio, USA) pH electrode. Based on the linear behaviour of the buffer pH to the neutralized acidity, the equivalent amount of lime can be calculated. Known values of lime requirement from soil incubation studies were related to the soil buffer pH after extraction. The amount of ground limestone needed to be applied to the soil to reach the crop specific target value can then be looked up in tables based on these experiments (McLean, 1982; Shoemaker et al., 1961).

The percentage OM (w/w) was determined by loss on ignition using 5 g of sample weighed into a crucible and dried at 105 °C to remove capillary water. Samples and crucibles were then weighed and put into a furnace at 500 °C for 12 h and the loss on ignition determined by comparing the weights.

Particle size distribution was determined on a composite sample for each field to describe the texture class at each field. They were analysed with the sieve pipette method using 20 g samples for the USDA particle size classification (Gee and Bauder, 1986; Massey et al., 2007). The organic matter in the sample was removed by oxidizing it with hydrogen peroxide, after which the clay aggregates were dispersed with sodium hexametaphosphate. The dispersed sample was then sieved with a 50 μm sieve to retain the sand fraction. The silt and clay fractions were determined through sedimentation.

3.1. Spectral data acquisition

A subsample of each of the 655 field samples was ball milled at a frequency of 25/s for three minutes and 1 g of the milled soil was filled into a sample cup (diameter 10 mm) and the surface smoothed with a blade. Spectral samples were prepared in triplicate for each soil. Samples were loaded onto the sample tray using a PIKE Technologies "AutoDiff" auto sampler (PIKE Technologies, Madison, WI, USA). MIR spectra were collected using a Perkin Elmer "Spectrum 400 FT-IR" spectrophotometer (Perkin Elmer, Inc. Waltham, MA, USA) with KBr beam splitter and nitrogen cooled mercury cadmium telluride (MCT) detector in diffuse reflectance mode. The samples were scanned in the MIR range from 4000–450 cm^{-1} in a 2 cm^{-1} sampling interval and are reported smoothed at a resolution of 4 cm^{-1}. 16 scans of each sample cup were made and averaged and the results are displayed in absorbance units (A = $\log_{10}(1/R)$, R = reflectance) (Esbensen and Swarbrick, 2018; Sherman Hsu, 1997). Before every run of 60 samples, the background was calibrated with a silicon carbide reference disk

3.2. Chemometric calibration and validation

Triplicate spectra of each sample were analysed for their uniformity by calculating the overall standard deviation of the repeats. First the standard deviation in each wavenumber of the triplicates was calculated, then, the standard deviation of the values of all standard deviations was calculated. A threshold value of 0.1 was set differences to establish the criteria for removing spectral reps from the dataset. None of the scanned samples exceeded the threshold criterion and all samples were kept for further processing. Triplicate spectra were then averaged to reduce signal to noise ratio, and averaged spectra brought forward for pre-processing and analysis.

For the spectral calibration, MIR spectra and their corresponding laboratory data were loaded in the UNSCRAMBLER X software. The dataset was split into a calibration set (ca.75% of the data) and validation set (ca. 25% of the data). The random selection was carried out on a field basis, so that samples from 31 fields (495 samples) were assigned to the calibration, and samples from 10 fields (160 samples) were assigned to the validation dataset. The calibration set was then used to research the best pre-treatment options for the LR prediction with PLSR. The calibration set was loaded in the model with 10 LVs to
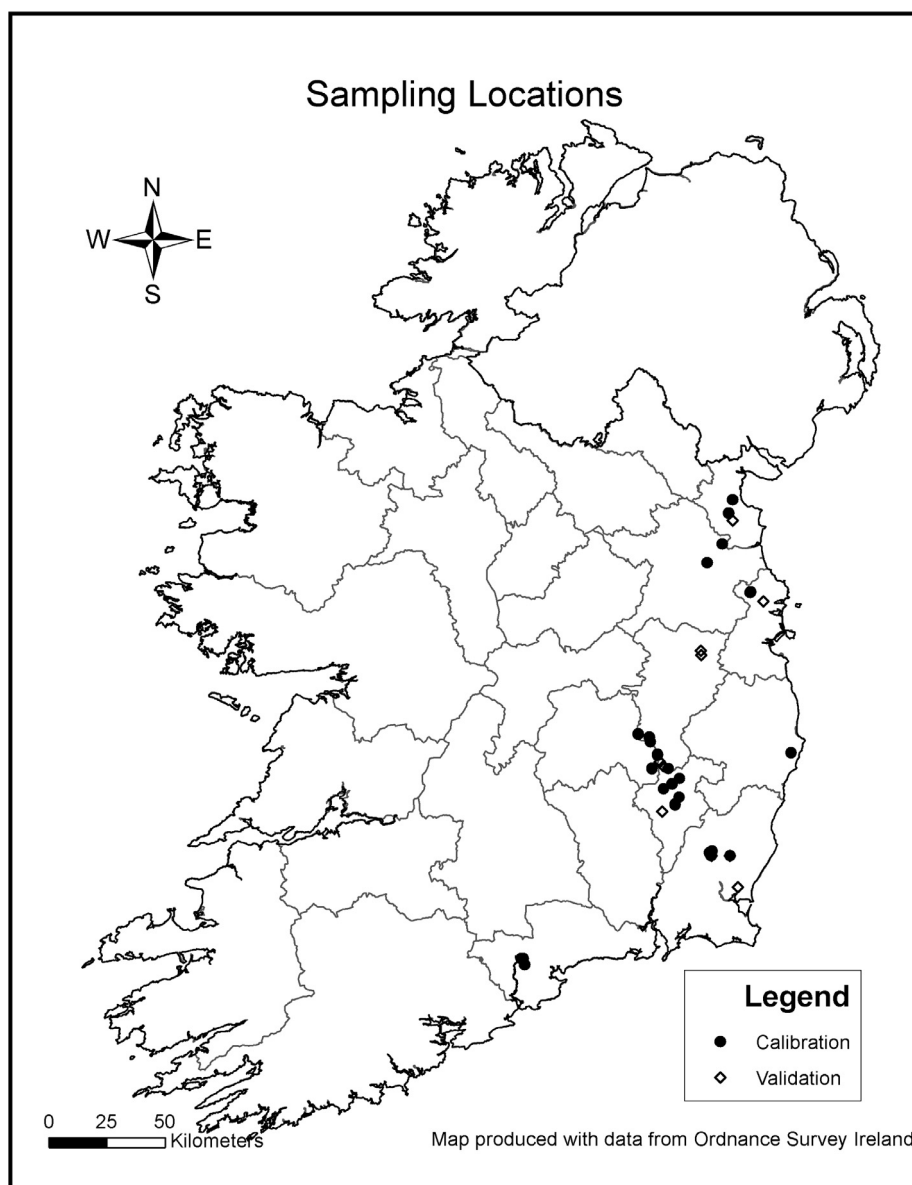
Fig. 1. Sites selected for sampling, with calibration (filled) and validation (open) fields indicated.

be calculated. To get a better estimate of the model, a 20-fold random cross-validation (bin size: 24 samples) was applied.

Different combinations of pre-treatments including trimming, smoothing, Savitzky-Golay smoothing, mean centring, Savitzky-Golay derivatives, MSC and SNV were applied to the spectra which were then used in a PLSR run. From these runs, the model performance parameters R^2, RMSE and the optimal number of LVs needed was used as a selection criterion for the pre-treatment. The goal hereby was to maximize the R^2, minimize the RMSE and keep the model as parsimonious as possible (minimize number of LVs). Theoretically the R^2 can be increased to reach close to 1 with additional LVs, but very often this leads to an increase in RMSE and model overfitting. set.

The goodness of the prediction was evaluated with the a set of performance indicators: the R^2 value describing the amount of the variance explained by the model, the root mean square error of prediction RMSEP, the bias describing the mean error (Esbensen and Swarbrick, 2018), the ratio of performance to interquartile range IQR (RPIQ), which is calculated as the fraction of the interquartile range of the laboratory data (Q3-Q1, quantifying the spread of the central 50% of the data) and the RMSEP (RPIQ = IQR/RMSEP) (Bellon-Maurel

et al., 2010; O'Rourke et al., 2016) and the ratio of performance to deviation RPD, which is calculated as the fraction of the standard deviation of the laboratory data (SD) and the RMSEP (RPD = SD/RMSEP) (Chang et al., 2001). The last two indicators are used in spectroscopic literature to make data more comparable, accounting for the differences in the spread of the data. Their explanatory power to classify the model performance is the same as the R^2 (Minasny and McBratney, 2013), but useful to compare datasets with different spreads of data, with the advantage of the RPIQ being able to handle skewed data (Bellon-Maurel et al., 2010).

4. Results and discussion

4.1. Field/soil description

Five Great Soil Groups from the Irish Soil Information System (Simo et al., 2007) were represented in the data, with Luvisols and Brown Earths recorded at 21 and 12 fields, respectively. These soil types, especially Luvisols are generally favouring tillage operations (Blume et al., 2010). Other Great Soil Groups represented across the fields

Table 1
Summary statistics for the laboratory values of OM (loss on ignition), pH (water) and LR (SMP) and texture classes by field.

	OM [%]	pH	LR [t/ha]	Texture by field		
Min	2.0	5.0	−10.5	USDA texture class	n (fields)	%
Max	10.2	8.2	10.0	sandy loam	16	39%
Average	5.8	6.6	−3.0	loam	18	44%
Median	5.6	6.6	−2.5	clay loam	6	15%
Range	8.3	3.2	20.5	sandy clay loam	1	2%

included Groundwater Gley (1 field), Surface Water Gley (2 fields), Brown Podzolic (2 fields) and Alluvial Soil (1 field).

The summary statistics of the laboratory values (see Table 1) show ranges of OM from 1.9% to 10.2%, of pH between 5 and 8.2 and LR from −10.5 to 10 t/ha, with the negative values meaning that the fields do not need lime to bring the pH to favourable levels. Field composites were described by four USDA texture classes: the majority of the fields were described as loam (18 fields) and sandy loam (16 fields), with clay loam being found in six fields and one field recorded as sandy clay loam.

Closer examination of the LR data showed that around 75% of the samples had a LR less than or equal than zero. Examining the pH values, around 60% of the samples had a pH value of 6.5 or higher (target value for cereals in tillage fields (The Fertilizer Association of Ireland, 2016)). In a report from the Professional Agricultural Analysis Group (Professional Agricultural Analysis Group, 2016) about soil analysis data from soil laboratories around the United Kingdom an average pH value for tillage samples (n = 64,000) of 6.73 was found. 40% had a pH value under the target value of 6.5. These values are in line with the findings of the current study. Consulting the database for soil fertility in Ireland in 2018 (Teagasc, 2018) the same behaviour is visible, with 65% of the samples from tillage being above pH 6.5. For liming advice the negative values are simply reported as "no LR", but in this research the actual values will be used as they are measuring a response to the SMP buffer, and hence it will increase the range of the calibration.

4.2. Calibration

Examples of raw spectra for three fields with maximum, minimum and zero LR are presented in Fig. 2 with regions of known absorptions of soil parameters indicated in the graph.

Spectral pre-treatment for the best calibration consisted of trimming the spectra at 650 cm^{-1}, Savitzky-Golay smoothing (polynomial order: 2, smoothing window: 11 points) and SNV. Using 6 LVs, the model produced an R^2 of 0.87, a root mean squared error of cross validation (RMSECV) of 1.55 t/ha, a bias of 0.01 and a RPIQ of 5.1. No considerable improvement in adding more latent variables after LV6 was achieved, and further addition of LVs would over-fit the model. The pre-treatment of the spectra improved the model performance considerably, R^2 was increased from 0.75 to 0.87 while the RMSECV decreased from > 2 to 1.55 t/ha using the same number of LVs. The number of LVs was considerable lower than the eleven described by Viscarra Rossel et al. (2001). In their calibration they could reach an RMSE of 0.6 t/ha which is considerable lower than that in the present study. This can be explained by the fact that they used 122 samples from one field, while our study encompassed 41 fields and only 16 points per field.

In addition to the subdivision of the full dataset into calibration and validation (by field), it was also grouped by texture class, to examine its effect on the model performance. The only sandy clay loam field was re-assigned to the group of sandy loam (n = 271). This decision is justified, as the sandy clay loam sample contains 20.5% clay, which is only 0.5% above the threshold between sandy loam and clay loam.

The other two groups were loam (n = 288) and clay loam (n = 96).

From the sandy loam and the loam datasets, 25% of the samples (in this case randomly selected from the 271 and 288 data points respectively), were held back for validation, while the clay loam dataset was only modeled with cross-validation due to the lower number of samples.

Using the same pre-treatment options, the subsets by texture class didn't show considerable improvements in the model, conversely, the number of LVs increased to 7 for the sandy loam subset, to 8 for the loam subset, and to 10 for the cross-validated clay loam subset. The R2 was with 0.91 slightly higher for the loam subset, for sandy loam and clay loam they were slightly lower with 0.83 and 0.81 respectively. For the RMSECV, the subsets showed lower values with 1.51 t/ha for the sandy loam subset and 1.26 t/ha for the loam subset. The clay loam subset exhibited with 0.86 t/ha a considerably lower value than the rest. This pattern wasn't displayed in the RPIQs, which were all lower than the value for the entire dataset, ranging from 4.4 for the loam subset to 3.0 for the clay loam subset. The different behaviour of RMSECV and RPIQ shows that more than one statistical measure has to be used to assess the model performance (Hutengs et al., 2019).

Spectral scores and loading weights provided some insight into the drivers behind the calibration model. Fig. 3a shows the scores grouped by texture class for LV1 vs. LV2. Here a clear trend in clay content can be seen to be positively correlated with LV1. Taking the loading weight for LV I into consideration (Fig. 4), this connection between clay content and LV1 is seen in strong positive peaks in areas where absorptions for clay have been recorded in previous studies (Janik et al., 1998; Nocita et al., 2015; Soriano-Disla et al., 2014; Stenberg and Viscarra Rossel, 2010; Vohland et al., 2014). LV1 describes 46% of the variance in the laboratory dataset and 69% in the spectra respectively, therefore representing half of the variance in the model compared to LV2 (20% of laboratory variance and 4% of spectral variance explained). The discrepancy in variance described for LV2 could be also linked to the strong peak in the loading weights for LV2 at 1320 cm^{-1}, a waveband where no distinct absorptions for soils have been reported in the literature. It can be linked to an absorbing feature of carbonates (1295 cm^{-1}) (Bruckman and Wriessnig, 2013) or silica which was distorted by specular reflectance (1360 cm^{-1}) (Reeves et al., 2005)This peak falls into a region where generally complex OM absorbs IR radiation, but inspecting LV2 in the score plot for OM didńt show clear trends. Interestingly this distinct peak is also visible in Viscarra Rossel et al. (2001), once as negative valley for LV1 and positive peak in LV3. By examining the plot grouped by pH (pH laboratory values split into the four quartiles Q1-Q4, Fig. 3b), a slight negative correlation was observed, pointing to the pH value influencing the second LV. The loading weights for LV2 (Fig. 5) were described by positive peaks for 2:1 clay minerals associated with higher CEC than kaolinite (Blume et al., 2010) and a negative peak for carbonates

4.3. Validation – total dataset and single field prediction

The model was applied to the data retained for validation, which was compiled as a single dataset of 160 samples, and also as a field database using ten fields with 16 samples per field retained for field scale validation. The results of the prediction are displayed in Table 2, with the entire prediction set producing a R2 of 0.76, an RMSEP of 1.68 t/ha and an RPIQ of 3.58. The R2 decreased considerably compared to the result of 0.87 in the calibration set, while the RMSEP didn't increase to the same extent. The values for the predictions of the single fields are in table SI1 and varied with R2 between < 0.2 to 0.72, RMSEP from 3.22 to 0.74 t/ha LR, and for RPIQ from 0.4 to 3.6. The fields with the best performance were field 5 and field 40, whereas field 8, 21 and 33 have very low R2 and RPIQ, and very high RMSEP values. The predicted vs. reference plot for all fields of the prediction set is displayed in Fig. 6.
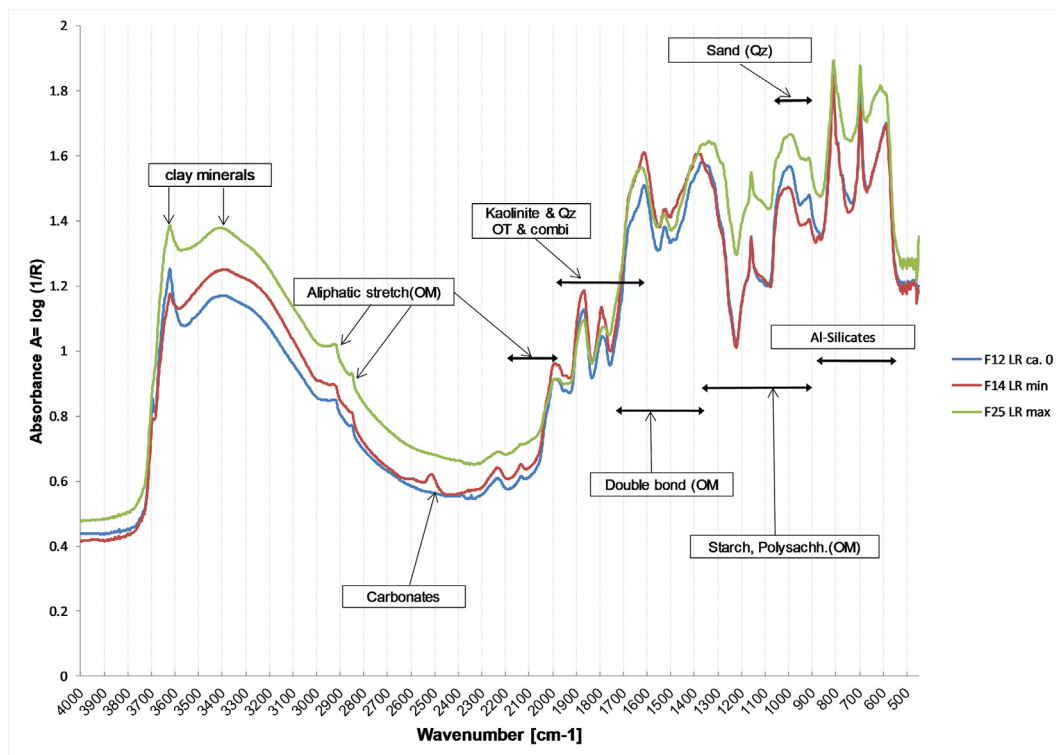
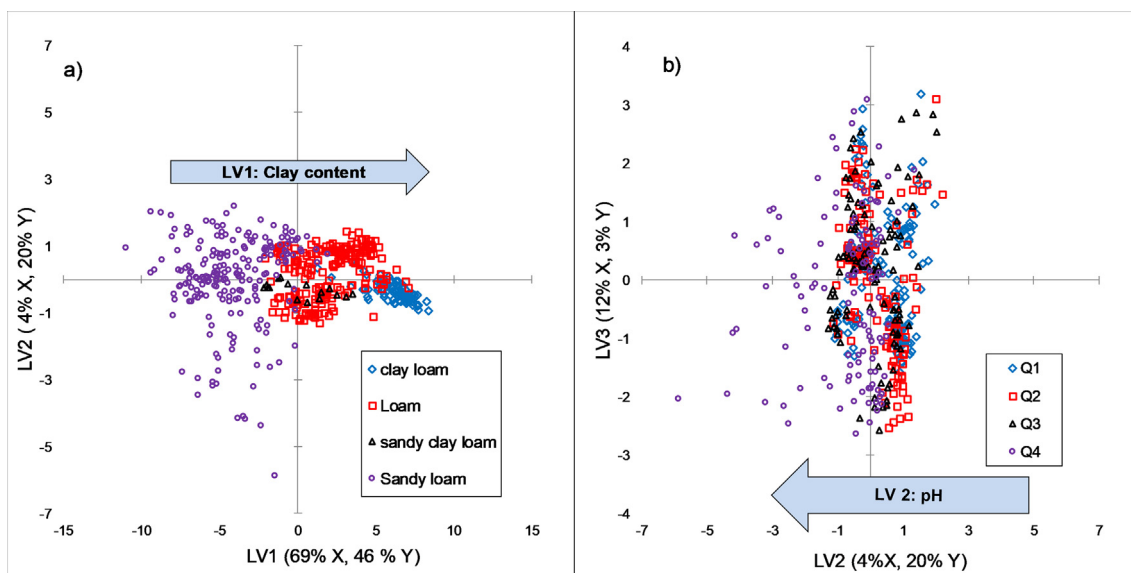**Fig. 2.** Raw spectra for minimum, maximum and zero lime requirements with regions of known absorption indicated.

Fig. 3. Score plots of a) LV1 vs. LV2, grouped by texture class and b) LV2 vs. LV3 grouped by quartiles of pH.

4.4. Validation – prediction for subsets by texture class

The prediction of the validation subsets for sandy loam and loam were better compared to prediction derived from the entire dataset. For the sandy loam subset, the R^2 of 0.86 was higher than in the calibration subset (0.83), for the loam subset it was with 0.85 still higher than the overall prediction R^2 of 0.76. The RMSEs were in the same order of magnitude as in the whole prediction with 1.22 t/ha for the sandy loam and 1.40 for the loam subset respectively. These slightly better performance indicators come at the cost of one and two more LVs, making the model less parsimonious. Regarding the relative model performance indicator RPIQ, the sandy loam subset with RPIQ 4.5 showed a higher value than its calibration set, whereas the loam subset performed slightly worse with 3.9. Compared to the entire validation set both subsets performed better.

The slight improvement of the model parameters when subdividing the dataset by texture class, in conjunction with the increased number of LVs indicates that there would be no significant gain in information by testing the sample for texture class first and applying texture-specific models.

The prediction statistics presented here are in a similar range reported by Janik et al. (1998) and Merry and Janik (1999) for a data set for 180 Australian soils where LR was predicted from land uses and soil types. The soils in our study are all from the same land use, and LR values are typical for tillage soils in Ireland (Teagasc, 2018) and the United Kingdom (Professional Agricultural Analysis Group, 2016).
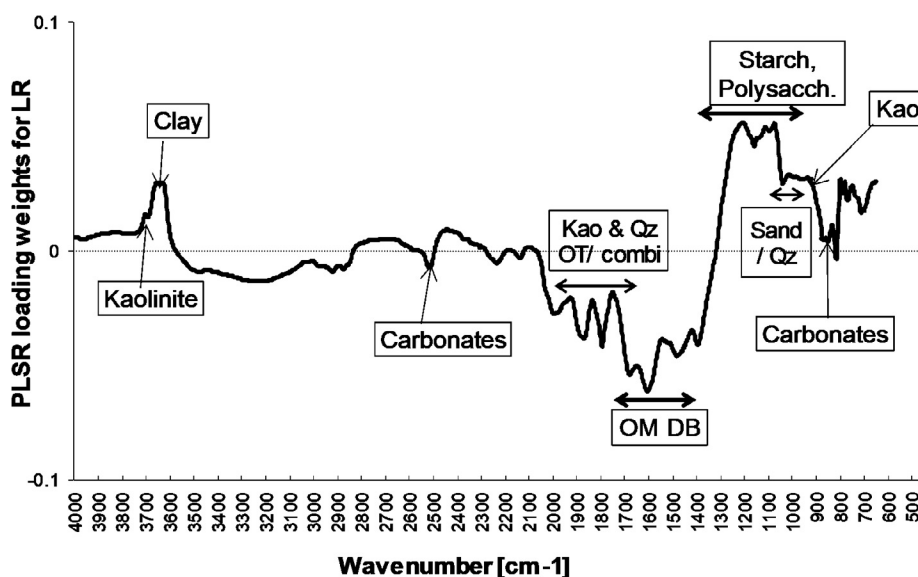
Fig. 4. Loading weights for LV1 with peaks for various soil components highlighted (Kao: kaolinite, Qz: quartz, OT: overtones, combi: combination bands, OM DB: organic matter double bonds).

To investigate the accuracy of the spectral calibrations for use as an alternative to the current laboratory SMP method the predicted values for each field (16 samples per field) were used to calculate a field average. This average was compared to the average of the laboratory values. The results in Table 3 show the difference between MIR predictions and laboratory values from 0.25 t/ha LR in field 5 up to 1.5 t/ha for field 8.

4.5. Model performance indicators

The RPIQ (as well as the RPD) are widely used in soil spectroscopy and various classifications are applied to categorize model performance into "good" and "bad". The thresholds for the classes often vary among different authors, and all attempts give arbitrary thresholds (Minasny and McBratney, 2013). However, these parameters are used to describe the relationship between the spread of the data (be it SD or IQR) and the error of prediction. Hence, an RPIQ of 2 describes a prediction, where the error of prediction is half of the spread of 50% of the data around the median. To examine the predictive power of the MIR models

at single field scale and to get a better grasp of the desired precision of the model, an additional performance parameter was used. It calculates the ratio of the range of the whole dataset to the error including a 95% confidence interval (Esbensen and Swarbrick, 2018; Naes et al., 2004) with an equation similar to the RER (RER = range/RMSE) (Fearn, 2002) which results in the following equation

$$(max - -min)/2 * RMSE.$$

This approach quantifies the prediction uncertainty as well as the desired level of accuracy and is useful when a number of samples was taken and their average is formed, as it is the case in the single field predictions. With this parameter it can be evaluated if the predicted value with the confidence interval lies within the spread of the laboratory data. If the value is > 1 it indicates, that the spread of the lab dataset is bigger than the prediction interval, justifying the use of predicted values. As displayed in Table 3, the parameter shows that, in the case of the predicted validation fields a spectral prediction is justified.
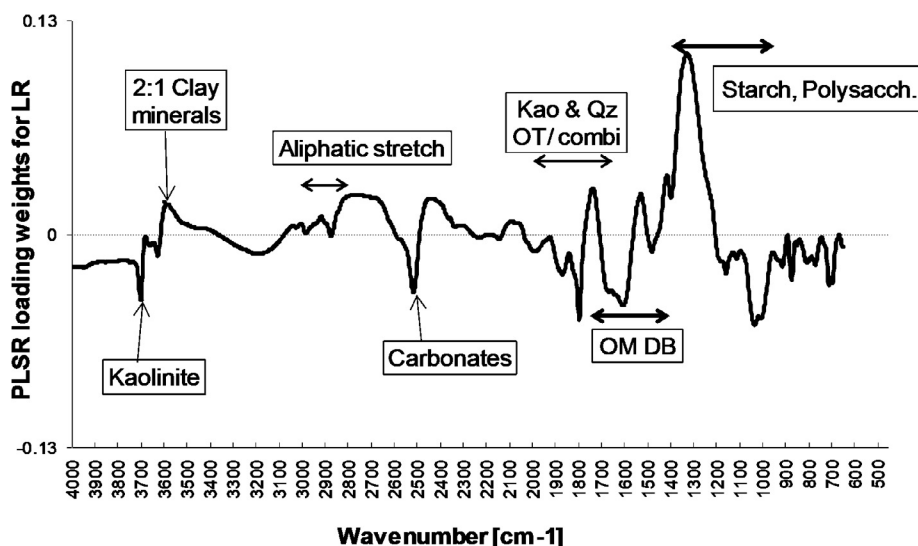

Fig. 5. Loading weights for LV2 with peaks for various soil components highlighted (Kao: kaolinite, Qz: quartz, OT: overtones, combi: combination bands, OM DB: organic matter double bonds).

Table 2

Summary stats and prediction results with the coefficient of determination (R^2), root mean square error of prediction (RMSEP/CV) or cross-validation, standard error of prediction or cross-validation (SEP/CV) bias, the ratio of performance to IQR (RPIQ = IQR/RMSE), the ratio of performance to deviation RPD (RPD = SD/RMSE), model bias and the number of latent variables used by the model for overall calibration and validation set and calibration and validation grouped by texture class.

	Calibration all	Validation all	Sandy Loam cal	Sandy Loam val	Loam cal	Loam val	Clay Loam (Xval)
Summary statistics (lab)							
n	459	160	203	68	216	72	69
Q1	−7.0	−7.0	−8.3	−8.5	−4.5	−4.5	−1.1
Q3	0.9	−1.0	−2.5	−3.0	1.0	1.0	1.5
min	−10.5	−9.5	−10.5	−10.0	−9.5	−9.0	−4.0
max	10.0	4.0	5.5	1.0	10.0	8.0	4.5
median	−2.0	−3.5	−6.0	−6.0	−1.5	−1.5	0.0
SD	4.3	3.4	3.7	3.3	4.2	3.6	1.9
range	20.5	13.5	16.0	11.0	19.5	17.0	8.5
IQR	7.9	6.0	5.8	5.5	5.5	5.5	2.6
Model Performances							
R^2	0.87	0.76	0.83	0.86	0.91	0.85	0.81
RMSEP/CV	1.55	1.68	1.51	1.22	1.26	1.40	0.86
SEP/CV	1.56	1.68	1.51	1.22	1.26	1.40	0.86
Bias	0.01	0.05	0.018	0.015	0.015	−0.145	−0.04
LVs	6	6	7	7	8	8	10
RPIQ	5.08	3.58	3.81	4.51	4.37	3.93	3.05
RPD	2.79	2.06	2.46	2.73	3.30	2.56	2.26
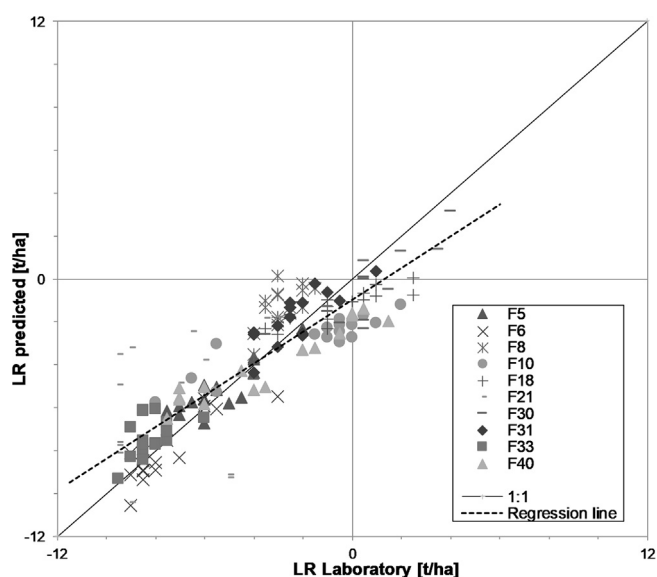
Fig. 6. Laboratory LR (SMP) vs. predicted (MIR) values of the prediction set, marked by field and overall R^2 and RMSEP.

Table 3

field averages for laboratory and predicted LR and the difference between the two methods and the range/2*RMSE as a metric for the precision of the prediction.

Field #	Average LR lab [t/ha] ± SD	Average LR prediction [t/ha]	Difference Laboratory-prediction (abs)	Range/ 2*RMSE
5	−5.44 ± 1.4	−5.19	0.25	2.02
6	−7.53 ± 1.6	−8.02	0.49	2.85
8	−2.84 ± 0.7	−1.34	1.50	2.09
10	−1.72 ± 2.9	−2.86	1.14	10.58
18	−0.69 ± 1.9	−1.36	0.67	4.34
21	−7.50 ± 2.3	−6.06	1.44	10.46
30	−0.06 ± 2.2	−0.98	0.92	5.63
31	−2.22 ± 1.3	−1.86	0.36	2.27
33	−8.19 ± 0.8	−7.38	0.81	2.07
40	−3.41 ± 3.0	−4.00	0.60	7.43

4.6. Implications on current practices of LR determinations

Current practice of lime application on farms, required applications of lime every five years, mostly spread in one blanket application where rates are often based on estimates from crop offtakes and fertilizer application (0.2 t/ha lime per 100 kg nitrogen fertilizer applied, 15 kg lime/t cereal offtake) (The Fertilizer Association of Ireland, 2016). Taking into consideration the variability of LR in a field (see Table 2) and the current blanket application of lime, the alternative MIR derived LR based on averages is a faster and safer alternative at this level of accuracy to current methods using potassium chromate (SHVC). Fig. 7 visualizes the precision of the average on the example of one field.

The SMP buffer LR has been compared with other methods in the USA (Sikora buffer, $Ca(OH)_2$ titration, Mehlich buffer) and the UK (RothLime model), and Tunney et al. (2010) reported R^2 values between SMP LR and similar methods ranging from 0.7 to 0.84. The MIR prediction provided a value for R^2 of 0.76 for the entire prediction set, which lies in the range of values comparing laboratory-based tests, indicating that the MIR model is as good as the laboratory alternatives at replacing the SMP extraction for future LR measurements.

Merry et al. (Merry and Janik, 1999) used the predicted LR to derive a LR map of an area of 50 × 50 km. For field sizes of 2–37 ha as in our research, the accuracy of the prediction isn't precise enough (yet). But the potential for predicting other soil parameters (e.g. particle size, OM, pH, CEC) with the same MIR scan offers an opportunity for future applications. As it can be seen in the loading weights (Fig. 4&5), there are clear signals for components which are influencing the LR, which means that the MIR spectrum indeed can be used to predict LR.

5. Conclusions

Soil samples from tillage fields in Ireland were analysed for LR with the SMP buffer method in the laboratory and a spectral calibration with PLSR was developed from MIR scans of the samples. By examining the loading weights, clear signals for soil parameters influencing the LR could be found as drivers for the model. This shows that MIR spectroscopy is capable of detecting the LR in soils. With an RMSEP of 1.68 t/ha the precision of the PLSR model is not sufficient to predict the spatial variability of LR within the field for most single field predictions. When the prediction values for one field are averaged, the results lie close to the laboratory averages. This indicates that MIR spectroscopy can be used to estimate an average LR as a substitute for the SMP buffer method, and with future research it can be optimized to be used in
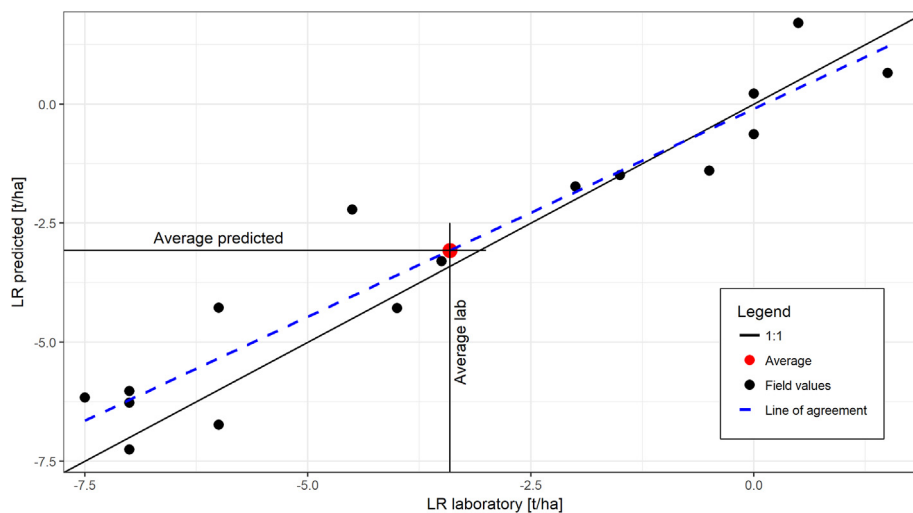
Fig. 7. Calculated LR averages from laboratory and MIR predicted values for field 40.

precision agriculture. This study forms the basis for a fast and cheap substitute for lab analyses of LR, especially as information about other important soil parameters are contained in the same spectrum, which can be predicted simultaneously.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2020.114171.

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