

# Rapid determination of lime requirement by mid-infrared spectroscopy: A promising approach for precision agriculture

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## Abstract

Mid-infrared spectroscopy (MIRS) has proven to be a cost-effective, high throughput measurement technique for soil analysis. After multivariate calibration mid-infrared spectra can be used to predict various soil properties, some of which are related to lime requirement (LR). The objective of this study was to test the performance of MIRS for recommending variable rate liming on typical Central European soils in view of precision agriculture applications. In Germany, LR of arable topsoils is commonly derived from the parameters organic matter content (SOM), clay content, and soil pH ( $\text{CaCl}_2$ ) as recommended by the Association of German Agricultural Analytical and Research Institutes (VDLUFA). We analysed a total of 458 samples from six locations across Germany, which all revealed large within-field soil heterogeneity. Calcareous topsoils were observed at some positions of three locations (79 samples). To exclude such samples from LR determination, peak height at  $2513\text{ cm}^{-1}$  of the MIR spectrum was used for identification. Spectra-based identification was accurate for carbonate contents  $> 0.5\%$ . Subsequent LR derivation ( $\text{LR}_{\text{SPP}}$ ) from MIRS-PLSR predictions of SOM, clay, and pH ( $\text{CaCl}_2$ ) for non-calcareous soil samples using the VDLUFA look-up tables was successful for all locations ( $R^2 = 0.54\text{--}0.82$ ;  $\text{RMSE} = 857\text{--}1414\text{ kg CaO ha}^{-1}$ ). Alternatively, we tested direct LR prediction ( $\text{LR}_{\text{DP}}$ ) by MIRS-PLSR and also achieved satisfactory performance ( $R^2 = 0.52\text{--}0.77$ ;  $\text{RMSE} = 811\text{--}1420\text{ kg CaO ha}^{-1}$ ;  $\text{RPD} = 1.44\text{--}2.08$ ). Further improvement was achieved by refining the VDLUFA tables towards a stepless algorithm. It can be concluded that MIRS provides a promising approach for precise LR estimation on heterogeneous arable fields. Large sample numbers can be processed with low effort which is an essential prerequisite for variable rate liming in precision agriculture.

**Key words:** calcite / dolomite / partial least squares regression / soil acidification / soil heterogeneity / soil sensing / variable rate fertilization

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## 1 Introduction

Soil acidification is a natural process that is aggravated by application of certain fertilizers (Goulding, 2016). Liming counteracts soil acidification. Besides the neutralization of acids, liming has various far reaching impacts on soil structure as well as on nutrient availability (Holland et al., 2018; Frank et al., 2019). Thus, for economic and agronomic reasons recommendations for optimum pH values exist in most countries (Edmeades et al., 1985; Goulding, 2016; VDLUFA, 2000a). The extent of soil acidification as well as the extent and rate of pH rise after liming depend on various soil properties such as clay and organic matter content (Robson, 2012; Bloom et al., 2005).

In Germany, the Association of German Agricultural Analytical and Research Institutes (VDLUFA) published a recommendation algorithm that comprises the following steps (VDLUFA, 2000a). Firstly, a target pH value with respect to management (arable land or permanent grassland), soil texture (clay content), and SOM content is defined. Secondly, the actual soil

pH value is measured. Thirdly, lime dosage is derived from the difference between target and actual pH value and given in  $\text{kg CaO ha}^{-1}$ , irrespective of the type of lime finally applied. The scheme for arable soils is organized in look-up tables where SOM contents and soil texture are grouped in only five and six classes, respectively (VDLUFA, 2000b). Main reasons for the coarse classification are that (1) clay and SOM are mostly not analyzed but estimated and (2) the algorithm should be simple, clear, and trustworthy for practitioners. The actual pH is classified into five classes (A: very low; B: low; C: optimal; D: high; E: very high). Despite rough classification of input parameters, the measurement of actual pH has to be precise, because a pH difference of 0.1 units can induce changes in lime recommendation up to  $2000\text{ kg CaO ha}^{-1}$ .

In agricultural practice in Germany and many other countries, soil testing is mostly based on a single composite topsoil sample (0–30 cm depth) for an area of up to three hectares. Consequently, within-field soil heterogeneity is not adequately



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considered (Robertson et al., 1993; Patzold et al., 2008; Wallor et al., 2018). Thus, the common practice easily leads to erroneous lime dosage on the sub-plot scale. Severe errors may particularly occur if fields have both calcareous and non-calcareous areas, because mixing of calcareous and non-calcareous sub-samples causes the entire composite sample to be calcareous and diminishes the recommended liming for the whole area to zero.

During the last decade, sensor based soil data acquisition and related precision farming applications made enormous progress (Gebbers and Adamchuk, 2010; Kuang et al., 2012). Infrared spectroscopy has potential for fast and precise quantification of various soil properties with minimum effort (Viscarra Rossel et al., 2006; Hutengs et al., 2018). Meanwhile, near-infrared (NIRS), visible-near infrared (vis-NIRS) as well as mid-infrared spectroscopy (MIRS) can replace or at least complement conventional laboratory methods for analyzing a wide range of soil properties (Bellon-Maurel and McBratney, 2011; Soriano-Disla et al., 2014). Compared to vis-NIRS, mid-infrared (MIR) spectra reveal more distinct features and thus show higher correlations with soil fertility parameters such as SOM and particle size distribution. However, vis-NIRS is already established for mobile measurements *in situ* (Mouazen et al., 2007; Rodionov et al., 2015), while portable MIRS devices have only recently become commercially available (Hutengs et al., 2018).

To derive soil properties from IR spectra, multivariate statistics, such as partial least squares regression (PLSR), are commonly applied. Prediction models for all relevant LR parameters (*i.e.*, SOM, soil texture, pH, and carbonate) have been successfully calibrated using PLSR (*e.g.*, Viscarra Rossel et al., 2006; Soriano-Disla et al., 2014). In some cases, even direct evaluation of mid-infrared spectral information is possible. Carbonates can be assigned to bands at 2686–2460  $\text{cm}^{-1}$ , 1850–1784  $\text{cm}^{-1}$ , 1567–1295  $\text{cm}^{-1}$ , 889–867  $\text{cm}^{-1}$ , 734–719  $\text{cm}^{-1}$ , 719–708  $\text{cm}^{-1}$ , and 2910–2850  $\text{cm}^{-1}$  (Mirzaeitalarposhti et al., 2016). In particular, the wavenumbers 2686–2460  $\text{cm}^{-1}$  and 889–867  $\text{cm}^{-1}$  are specific for carbonate in soil (Tatzber et al., 2010). Accordingly, Tatzber et al. (2007) successfully determined carbonate content in soil from the peak area of these two bands. However they did not take into account variations in spectral response of different carbonates.

Using MIRS and PLSR modelling, Janik et al. (1998) and Viscarra Rossel et al. (2006) proved successfully the potential of MIRS to determine lime requirement for low organic matter Australian soils. The study of Janik et al. (1998) was based on 188 samples from northern Australia, while the study of Viscarra Rossel et al. (2006) was based on 118 samples from one single arable field. For Canadian soils, cation exchange capacity (CEC) estimation and subsequent LR derivation were successfully demonstrated by Leblanc et al. (2016). However, in the latter study direct derivation of LR from MIR spectra failed.

In view of a future introduction to precision agriculture, the objective of this study is to explore more extensively the performance of MIRS and PLSR to derive variable lime recom-

mendations on field scale and thereby on various arable fields which reveal a large variability of soil characteristics within and between the fields in the context of the German standard LR algorithm.

The hypotheses of this study are:

- (1) Calcareous samples can be identified based on carbonate specific bands without evaluation of the whole spectrum prior to further LR evaluation.
- (2) The single parameters for determining LR (SOM, clay, and pH) can be predicted by MIRS in combination with PLSR.
- (3) Single parameter predictions (SPP) are suitable for subsequent derivation of precise lime requirement ( $\text{LR}_{\text{SPP}}$ ).
- (4) MIRS-PLSR can also be used to directly predict lime requirement ( $\text{LR}_{\text{DP}}$ ) in order to omit the detour *via* the single parameter determination according to the VDLUFA scheme.

To test the hypotheses, we investigated MIRS performance on 458 topsoil samples from six different locations in Germany. The chosen locations represented a wide range of soil parent materials as listed in the next section.

## 2 Material and methods

### 2.1 Test sites and sampling

Overall 458 arable topsoil samples (0–30 cm depth) from six locations in Western, Central, and Eastern Germany (see Tab. 1) were collected to test the potential of MIRS for the determination of lime requirement. The soils under study were classified as Cambisols, Stagnosols, Luvisols, Chernozems, Regosols, Arenosols, and Retisols according to the *IUSS Working Group WRB* (2015). At the locations Ascheberg (As), Bölingen (Bö), Hilberath (Hi) and Wilmersdorf (Wi), one field each was uniformly managed. At Görzig (Gö) and Heimbach (He), variable rate liming was conducted as part of fertilizer experiments. The chosen locations revealed large variability in soil texture, SOM content, and pH between and also within the locations (Tab. 2).

### 2.2 Ground Truth measurements and lime requirement (LR) recommendation

All samples were air-dried and sieved (< 2 mm) prior to reference (ground truth) measurements with those standard laboratory methods that are recommended by the VDLUFA. Soil texture classes were determined from particle size analyses that were conducted by the combined sieve and pipette method (*ISO 11277*, 2002). Total carbon content was determined after dry combustion (elemental analysis; *ISO 10694*, 1995). To determine inorganic carbon the gas-volumetric Scheibler method was used (*ISO 10693*, 2014). Soil organic matter content (SOM) was determined from the difference between total carbon and inorganic carbon multiplied by a factor of two (Pribyl, 2010). Soil pH was measured with a glass electrode in a 1:2.5 suspension of soil and 0.01 M  $\text{CaCl}_2$  (*ISO 10390*, 2005).

**Table 1:** Parent materials and reference soil groups (RSG according to *IUSS Working Group WRB*, 2015) at the six locations under study.

Location	Geographic setting	Parent material & reference soil group (RSG)
Ascheberg (As)	51°45'32"N, 7°34'47"E	Cretaceous marls partially covered by Saalian glacial till, aeolian sand, and fluvial sediments; RSG: Cambisols, Stagnosols
Bölingen (Bö)	50°34'1"N, 7°5'5"E	Pleistocene periglacial slope deposits consisting of (1) Devonian sand-, silt-, & claystones weathered during Mesozoic & Tertiary, (2) scattered Tertiary basalt bombs, and (3) Weichselian loess in variable amounts; RSG: Cambisols, Luvisols, Stagnosols
Görzig (Gö)	51°39'50"N, 11°59'48"E	Weichselian loess; RSG: Chernozems, Regosols
Heimbach (He)	50°37'13"N, 6°32'36"E	Pleistocene periglacial slope deposits consisting of weathered sand- and claystones from the Upper Bunter sandstone; RSG: Cambisols
Hilberath (Hi)	50°34'45"N, 6°59'27"E	Pleistocene periglacial slope deposits consisting of Devonian sand-, silt-, & claystones weathered during Mesozoic & Tertiary, partially covered by Weichselian loess; RSG: Cambisols, Stagnosols
Wilmersdorf (Wi)	53°6'39"N, 13°54'21"E	Weichselian glaciofluvial sands partly covering glacial till; RSG: Arenosols, Retisols, Luvisols, Planosols

Reference values for LR were calculated for all soil samples following the official algorithm of the *VDLUF*A (2000a, 2000b). Accordingly, soil texture was classified in five classes:  $\leq 5\%$ ,  $> 5\text{--}12\%$ ,  $> 12\text{--}17\%$ ,  $> 17\text{--}25\%$ , and  $> 25\%$  clay, respectively. Organic soils form a separate class were not relevant in this study. Further, SOM content was assigned to five classes:  $\leq 40$ , 41–80, 81–150, 151–300, and  $> 300$  g SOM kg<sup>-1</sup>, respectively. From the look-up table the respective target pH was determined. Finally LR was derived from the difference between the target and the measured pH value.

The *VDLUF*A algorithm was (1) applied as-is and (2) conceived as a continuous (*i.e.*, stepless) algorithm (in the following designated as refined *VDLUF*A). For this purpose, the original *VDLUF*A values for SOM and clay contents were interpolated in steps of 5 g kg<sup>-1</sup> and 0.5%, respectively.

### 2.3 Spectral features of calcite and dolomite containing soil samples

To investigate spectral features of carbonates in soil, reference loess loam material was mixed with different amounts of calcite and/or dolomite. The loess material originated from the Ap horizon of an arable field at the experimental farm of the University of Bonn at Klein-Altendorf. Both carbonates were purchased in defined quality from Alfa Aesar (Karlsruhe, Germany; ACS reagent grade). The carbonates were added in different quantities to the reference material in order to generate concentrations as follows: 2%, 5%, 10%, 20%, 40%, 60%, and 80% (w/w) of carbonates. In addition, the proportion of calcite to dolomite was varied in 0.2% steps in order to imitate spectral features of different calcareous soils. The reference material, pure calcite, and pure dolomite were investigated separately. The spectra of the resulting 89 samples were taken in the same way as for the other soil samples (see below).

### 2.4 Spectroscopic measurements

For MIRS measurements 2 g of each sample were ground in a ball mill. About 20 mg of the ground sample were divided in fivefold repetition into the hollowed positions of a microtiter plate and smoothed with a plunger. Diffuse reflectance mid-infrared Fourier transform (DRIFT) spectra were recorded in the laboratory with a Bruker Tensor 27 HTS-XT for automated high-throughput screening (Bruker Optik, Ettlingen, Germany). The device was operated with a liquid N<sub>2</sub> cooled mercury-cadmium telluride (MCT) detector and a broadband KBr beam splitter. For each spectrum 120 scans at a resolution of 4 cm<sup>-1</sup> and a spectral range of 7500–550 cm<sup>-1</sup> were carried out.

### 2.5 Spectra treatments and calibration of prediction models

The fivefold repeated spectra measurements were averaged in order to reduce noise. Furthermore, for multivariate data analysis the spectral range was narrowed to 3800–550 cm<sup>-1</sup>. Pre-tests had shown that data beyond 3800 cm<sup>-1</sup> were not relevant for our application. For chemometric modeling, the spectroscopy software OPUS Quant was used (Bruker Optik, Ettlingen, Germany). Partial least squares regression (PLSR) based on the PLS 1 algorithm (*Geladi and Kowalski*, 1986; *Martens and Næs*, 1989; *Wold et al.*, 1996; *Brereton*, 2018) was performed. For each location a separate prediction model was calibrated *via* leave-one-out cross validation (LOOCV). To avoid overoptimistic evaluation of LOOCV modeling results (*Bellon-Maurel and McBratney*, 2011), an additional test-set validation was performed for the locations with  $n > 70$  samples. Therefore, the sample set was divided in 70% for calibration and 30% for validation. The optimum number of latent variables for the prediction models was selected based on the smallest root mean square error of cross-validation (*RMSECV*) and root mean square error of prediction (*RMSEP*), respectively. To avoid over-fitting, the maximum number of latent variables was limited to ten. Five different methods for spectra preprocessing were tested to eliminate the physical effect of light scattering and to improve model

**Table 2:** Statistical summary of the observed soil properties at the six investigated locations; LR<sub>GT</sub> = lime requirement determined from ground truth, SD = standard deviation, CV = coefficient of variation (%).<sup>a</sup>

	Ascheberg <sup>(1)</sup> n = 39	Ascheberg <sup>(2)</sup> n = 76	Bölingen n = 71	Görzig <sup>(1)</sup> n = 20	Görzig <sup>(2)</sup> n = 92	Heimbach n = 62	Hilberath n = 39	Wilmsdorf <sup>(1)</sup> n = 20	Wilmsdorf <sup>(2)</sup> n = 39
<b>SOM (g kg<sup>-1</sup>)</b>									
mean (min–max)	36 (26–52)	35 (24–66)	25 (19–38)	36 (27–66)	33 (28–67)	28 (25–33)	29 (15–40)	21 (12–36)	18 (12–28)
SD; CV	6.4; 18	9.9; 28	4.5; 18	9.2; 25	3.3; 10	1.8; 6	5.2; 18	6.1; 29	4.2; 23
<b>Clay (%)</b>									
mean (min–max)	23 (10–55)	21 (9–51)	30 (18–57)	18 (5–21)	20 (15–23)	15 (11–19)	21 (14–27)	11 (5–18)	7 (2–12)
SD; CV	12; 52	11.6; 54	8.5; 29	3.6; 20	1.3; 7	2.0; 13	2.5; 12	4.0; 36	2.3; 31
<b>pH (CaCl<sub>2</sub>)</b>									
mean (min–max)	7.1 (5.9–7.4)	5.9 (4.5–7.3)	6.0 (5.1–6.5)	6.9 (6.5–7.3)	6.4 (5.6–7.1)	5.8 (4.5–6.7)	5.6 (4.4–6.3)	7.4 (6.7–7.8)	5.7 (4.4–7.0)
SD; CV	0.3; 5	0.6; 11	0.3; 5	0.2; 3	0.4; 6	0.6; 10	0.5; 8	0.3; 5	0.6; 11
<b>CaCO<sub>3</sub> (g kg<sup>-1</sup>)</b>									
mean (min–max)	32 (1–191)	0 (0–0)	0 (0–0)	4 (1–26)	0 (0–0)	0 (0–0)	0 (0–0)	16 (2–62)	0 (0–0)
SD; CV	41; 127			6; 155				17; 108	
<b>LR<sub>GT</sub> VDLUFA (kg CaO ha<sup>-1</sup>)</b>									
mean (min–max)	0 (0–0)	2889 (0–11100)	3869 (1700–9800)	0 (0–0)	2096 (0–5300)	3479 (0–9400)	5603 (1700–11700)	0 (0–0)	1531 (0–4900)
SD; CV		2294; 79	2056; 53		995; 47	2571; 74	2538; 45	0; 0	1350; 88
<b>LR<sub>GT</sub> refined VDLUFA (kg CaO ha<sup>-1</sup>)</b>									
mean (min–max)	0 (0–0)	2770 (0–10500)	3148 (1700–8300)	0 (0–0)	1633 (0–4100)	3142 (500–8300)	4900 (1600–11400)	0 (0–0)	1508 (0–4700)
SD; CV		2100; 76	1669; 53		811; 50	2311; 74	2479; 51		1270; 84

<sup>a</sup>Sample subsets: <sup>(1)</sup>calcareous samples, <sup>(2)</sup>non-calcareous samples.



accuracy (Varmuza and Filzmoser, 2009): none, first derivative, first derivative + standard normal variate (SNV), first derivative + multiplicative scatter correction (MSC), and second derivative. Preprocessing methods with the best predictive power were selected. Predictive power was evaluated by coefficient of determination ( $R^2$ ) between conventionally measured and predicted values and  $RMSECV$  or  $RMSEP$ . We also listed ratio of performance to deviation ( $RPD$ ) values because it is widespread, although it generally provides the same information as  $R^2$  (Minasny and McBratney, 2013). For evaluation,  $RPD$  was classified according to Viscarra Rossel et al. (2007):  $RPD < 1.0$  poor, 1.0–1.4 weak, 1.4–1.8 fair, 1.8–2.0 good, 2.0–2.5 very good, and  $\geq 2.5$  excellent prediction models; quantitative predictions are considered valuable for models with  $RPD$  values  $> 1.8$ . With respect to subsequent derivation of  $LR_{SPP}$ ,  $R^2$  and root mean square error ( $RMSE$ ) were calculated.

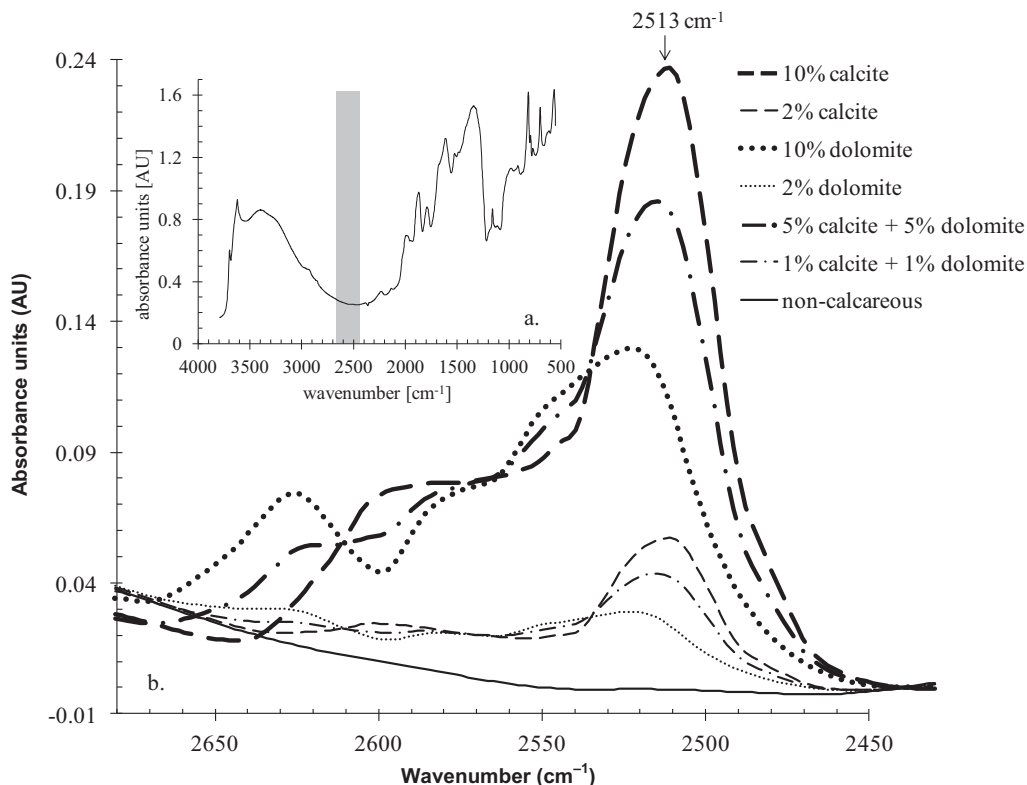
### 3 Results and discussion

#### 3.1 Identification of calcareous samples prior to $LR_{SPP}$ estimation

Mixing known amounts of pure carbonates (calcite and dolomite) with non-calcareous loess topsoil material caused peaks of variable height in specific bands in the MIR spectra. The strongest response occurred between  $2670\text{ cm}^{-1}$  and  $2450\text{ cm}^{-1}$  (Fig. 1). The same band was utilized by Tatzber et al. (2007). Yet, spectral features of calcite and dolomite

revealed important differences. Calcite induced a large peak at  $2513\text{ cm}^{-1}$ , while the dolomite peak appeared at  $2523\text{ cm}^{-1}$ ; a second smaller dolomite peak was located at  $2630\text{ cm}^{-1}$ . Shifts in bands for calcite and dolomite were also reported by Bruckman and Wriessnig (2013).

Besides wavelengths, also peak shapes varied: at equal carbonate contents, the major dolomite peak was less sharp. Note that this study was conducted with powdery pure minerals that were mixed with ground soil in variable quantity and combination. Spectral response of natural calcareous samples might deviate for several reasons. In nature, different carbonates with varying Ca/Mg ratio do occur. Further, signals from minerals coated with clay and/or SOM will be less clear and less quantitative. The same might apply for pedogenic (secondary) carbonates. However, we assume that the spectra shown in Fig. 1 represented the end-members of possible spectral shapes. In consequence, the characteristic features (Fig. 1b) were considered appropriate to separate non-calcareous samples from those containing calcite and/or dolomite. For our purposes, simple identification of carbonate presence was sufficient, because calcareous soils do not require liming irrespective of their carbonate content. Though, carbonate quantification from MIR spectra was successfully conducted by Tatzber et al. (2007) on the basis of peak areas in similar bands as identified in our study. However, the authors did not explicitly consider differences between different carbonates. Our results suggest that simple peak area quantification is perhaps defective if a sample contains different carbonates.



**Figure 1:** Mid-infrared spectra of (a) non-calcareous loess topsoil reference material for  $3800\text{--}550\text{ cm}^{-1}$  and (b) the same loess material after addition of variable amounts of calcite and dolomite. Note that (b) shows only the spectral range that was identified as carbonate specific.

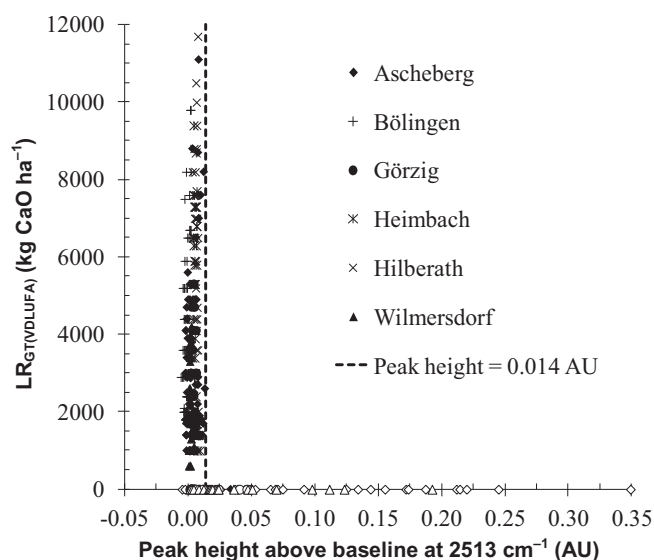
The height of absorbance at  $2513\text{ cm}^{-1}$  was successfully used to empirically identify soil samples that do not require liming (Fig. 2). After correction of baseline offset, peak height  $> 0.014$  absorption units (AU) at  $2513\text{ cm}^{-1}$  was considered an appropriate indicator for the presence of carbonate. Using this threshold, 96% of the samples with carbonate contents  $> 0.5\%$  were correctly identified. However, identification of carbonate contents  $< 0.5\%$  was less accurate, especially for dolomite containing samples, because the dolomite peak was less pronounced (Fig. 1). Four samples from the location As and one sample from Wi were erroneously classified as calcareous although being non-calcareous according to the HCl-pretest. The respective measured pH values varied between 6.75 and 7.25, revealing the known uncertainty of the Scheibler method at very low carbonate contents.

### 3.2 Prediction of SOM, clay, and pH prior to subsequent $\text{LR}_{\text{SPP}}$

Separate models for SOM, clay and pH prediction were calibrated via PLSR and LOOCV for subsequent LR determination (Tab. 3). For each location a specific model was created with the expectation to better consider prevailing soil conditions (Minasny et al., 2009). Especially with regard to pH prediction, local calibration is recommended, since the reasons for soil acidity may differ from location to location (Soriano-Disla et al., 2014). Consequently, merging geologically and pedologically different locations in a single model would yield worse prediction. In Tab. 3,  $R^2$ ,  $\text{RMSECV}$ , and  $\text{RPD}$  of LOOCV are summarized. The six local models for SOM, clay, and pH differed in performance but  $\text{RPD}$  was consistently good to excellent (Tab. 3).

**Table 3:** Model parameters for MIRS-PLSR prediction of soil properties that are required for determination of lime requirement: soil organic matter content (SOM), clay content and pH ( $\text{CaCl}_2$ ). Test-set validation was performed only for locations with  $n > 70$  samples; here, sample sets were randomly divided in 70% for calibration (not shown) and 30% for validation.  $R^2$ : coefficient of determination;  $\text{RMSECV}$ : root mean square error of cross validation;  $\text{RMSEP}$ : root mean square error of prediction for test-set validation;  $\text{RPD}$ : ratio of performance to deviation;  $\text{RPD}$  1.4–1.8 fair, 1.8–2.0 good, 2.0–2.5 very good,  $\geq 2.5$  excellent.

Location	$n$	SOM ( $\text{g kg}^{-1}$ )				Clay (%)				pH ( $\text{CaCl}_2$ )			
		$R^2$	$\text{RMSECV}$	$\text{RMSEP}$	$\text{RPD}$	$R^2$	$\text{RMSECV}$	$\text{RMSEP}$	$\text{RPD}$	$R^2$	$\text{RMSECV}$	$\text{RMSEP}$	$\text{RPD}$
Leave-one-out cross validation													
Ascheberg	115	0.93	2.4	–	3.65	0.98	1.7	–	6.74	0.90	0.25	–	3.23
Bölingen	71	0.95	1.0	–	4.35	0.98	1.3	–	6.55	0.70	0.17	–	1.83
Görzig	112	0.83	2.0	–	2.44	0.72	1.0	–	1.90	0.87	0.15	–	2.72
Heimbach	62	0.82	0.7	–	2.37	0.72	1.1	–	1.89	0.92	0.17	–	3.53
Hilberath	39	0.73	2.7	–	1.93	0.71	1.4	–	1.84	0.75	0.23	–	2.01
Wilmersdorf	59	0.92	1.4	–	3.63	0.91	1.0	–	3.26	0.90	0.30	–	3.22
Test-set validation													
Ascheberg	43	0.92	–	2.7	3.50	0.98	–	2.0	6.72	0.93	–	0.22	3.70
Bölingen	21	0.97	–	0.9	5.38	0.98	–	1.4	7.17	0.63	–	0.21	1.73
Görzig	33	0.79	–	2.2	2.19	0.67	–	1.0	1.75	0.88	–	0.14	2.84



**Figure 2:** Relationship between lime requirement derived from conventional SOM, clay, and pH analyses (ground truth;  $\text{LR}_{\text{GT}}$ ) and the height of the  $\text{CaCO}_3$  peak at  $2513\text{ cm}^{-1}$ . The calcareous samples from Ascheberg, Görzig, and Wilmersdorf are depicted as empty symbols. All other samples are non-calcareous and plotted with filled symbols. The peak height of 0.014 AU was empirically defined as threshold to classify samples as calcareous.

Test-set validation performance was largely equivalent to LOOCV (Tab. 3). However, in four out of nine cases LOOCV performed slightly better, confirming that LOOCV can sometimes be overoptimistic (Bellon-Maurel and McBratney, 2011). All in all, the calibration models were considered reliable to allow subsequent LR estimation.

Note that SOM and clay content can be reliably predicted with respect to IR-active functional groups and IR-active clay minerals, respectively. In contrast, pH can only be indirectly predicted due to correlations with other soil components, *i.e.*, CEC, exchangeable cations, and SOM composition). Soil acidity is controlled by several IR-active components (*e.g.*, proton-rich clays, Al oxyhydroxide minerals and sulfides, oxidizable ammonium and organic N as amides, and carboxylic acids and phenols) that finally allow pH prediction (Minasny *et al.*, 2009; Soriano-Disla *et al.*, 2014).

Varying model performance was consistent with the different extent of soil heterogeneity at the studied locations (Tab. 2). The surprisingly poor SOM prediction at Hi could be attributed to the former long-term use as pear orchard. It is assumed that a large variability in SOM quality occurred due to the presence of wooden root remains, and former herbicide stripes alternating with former grassed inter-row stripes. This went along with highly variable SOM quantity. Especially, particulate organic matter fractions can strongly impact MIR spectra (Bornemann *et al.*, 2010).

### 3.3 Determination of lime requirement after preceding single parameter MIRS predictions ( $LR_{SPP}$ )

For this approach, target pH and LR were picked from the look-up tables ( $LR_{SPP}$ ) after preceding separate MIRS prediction of SOM, clay, and pH and classification according to the VDLUFA scheme (VDLUFA, 2000a). All samples from B $\ddot{o}$ , He, Hi, and Wi had SOM contents  $\leq 40$  g kg $^{-1}$  (Tab. 2) and were grouped into the same class. In contrast, at As as well as at G $\ddot{o}$ , samples belonged to two SOM classes ( $\leq 40$  g kg $^{-1}$  and 41–80 g kg $^{-1}$ ). Prediction of SOM *via* MIRS led to correct class assignment of all samples from B $\ddot{o}$ , He, Hi, and Wi. Classification for As and G $\ddot{o}$  (SOM contents up to 66 g kg $^{-1}$  and 67 g kg $^{-1}$ , respectively) was correct in 95% and 88% of

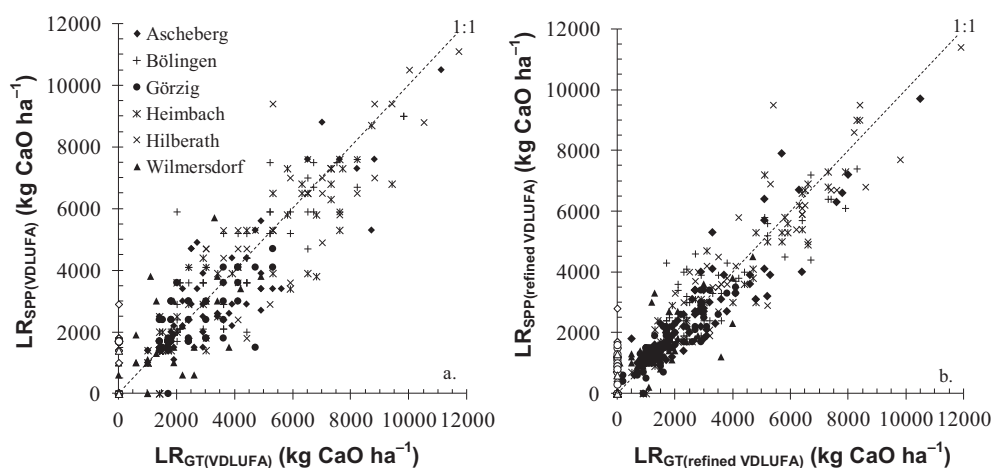
all cases, respectively. Erroneous classification occurred particularly for SOM contents close to the class boundaries (results not shown).

The SOM contents of the soils under study are representative for the majority of arable topsoils in Germany (Steinmann *et al.*, 2016). Within-field variability of SOM of the investigated soils was pronounced (Tab. 2) but can even be higher at other sites (Hbirkou *et al.*, 2012). However, in this study observed within-field variability in SOM contents had no or only little impact on recommended lime dosage because only two of the VDLUFA SOM classes were represented.

In contrast, clay content had a significant impact on target pH levels (Tab. 2) because five out of six VDLUFA texture classes were represented in this study. A considerable spatial variability of clay content—depending on occurring soil parent materials—was also observed within the fields. Predictions by MIRS achieved 90% concordance in assigning the samples to texture classes. Incorrect classification occurred only when clay contents were close to class boundaries. As mentioned before, this was observed for SOM classification as well. It is likely that incorrect classification happens also when applying the conventional procedure (texture-by-feel and SOM estimation by color).

Figure 3a shows the LR derived from conventionally measured data (ground truth,  $LR_{GT}$ ) versus  $LR_{SPP}$ . To conclude, separate MIRS predictions of the relevant parameters are generally appropriate for finally estimating LR.

It is evident that the VDLUFA algorithm produces abrupt changes in recommendation due to discretization. In particular, small variations in measured or predicted pH values cause large differences in liming recommendation. For example, a deviation as low as 0.1 pH units provokes variation of lime dosage up to 2000 kg CaO ha $^{-1}$ . However, in other countries similar classification schemes and look-up tables are



**Figure 3:** Lime requirement (LR) after conventional lab analyses (“ground truth”;  $LR_{GT}$ ) plotted against LR on the basis of soil properties as separately predicted *via* mid-infrared spectroscopy (MIRS) ( $LR_{SPP}$ ) (a) using the standard VDLUFA algorithm with soil organic matter and clay content classes and (b) using the refined, *i.e.*, stepless VDLUFA algorithm. Underlying MIRS prediction models were calibrated for each location by leave-one-out cross validation. Empty symbols represent calcareous samples from Ascheberg, Görzig, and Wilmersdorf.

applied (e.g., New Zealand: Edmeades et al., 1985; UK: Goulding, 2016). It is obvious that such rough look-up table schemes for LR estimation face methodological limits with respect to precision farming applications.

For that reason, the VDLUFA algorithm was refined by replacing the SOM and soil texture classes by a continuous function (refined VDLUFA; Fig. 3b). As expected, this reduced scattering around the 1:1 line between  $LR_{GT}$  and  $LR_{SPP}$  considerably (compare Fig. 3a, b). Improvement is also reflected by *RMSE* and  $R^2$  values (Tab. 4).

### 3.3.1 Erroneous $LR_{SPP}$ determination in calcareous samples

In both approaches (SPP original and refined) some samples were erroneously included in the MIRS- $LR_{SPP}$  calculations although they were calcareous as proven by the Scheibler method (Fig. 3a, b, empty symbols). The respective samples revealed measured pH < 7 at target pH  $\geq$  7 with respect to their clayey texture. It is supposed that these samples contained minuscule lime particles that were not dissolved during pH measurement. Spectral identification of these samples as calcareous had failed, most probably to very low carbonate contents and/or to weak spectral response of dolomite. From the methodological point of view, this is an uncertainty of the approach. However, in agricultural practice, liming these clayey soils is still appropriate in order to achieve the target pH value which was defined by the VDLUFA as optimum pH value. These high target pH values are necessary for clay rich soils in order to improve, e.g., soil structure (Frank et al., 2019). Liming would have at least no negative consequences on plant development in this case. Thus, sporadic false-positive liming recommendations at target pH  $\geq$  7 were not regarded as substantial procedural defect.

### 3.4 Direct prediction of lime requirement

To further reduce efforts for LR estimation, direct prediction was tested ( $LR_{DP}$ ). This approach aimed also to avoid accumulating errors from the individual single calibrations. Note that no preceding identification of lime presence was conducted in order to minimize efforts as far as possible. Indeed, models for  $LR_{DP}$  were successfully calibrated via LOOCV and close correlation between  $LR_{DP}$  and  $LR_{GT}$  was observed for all locations (Fig. 4a).

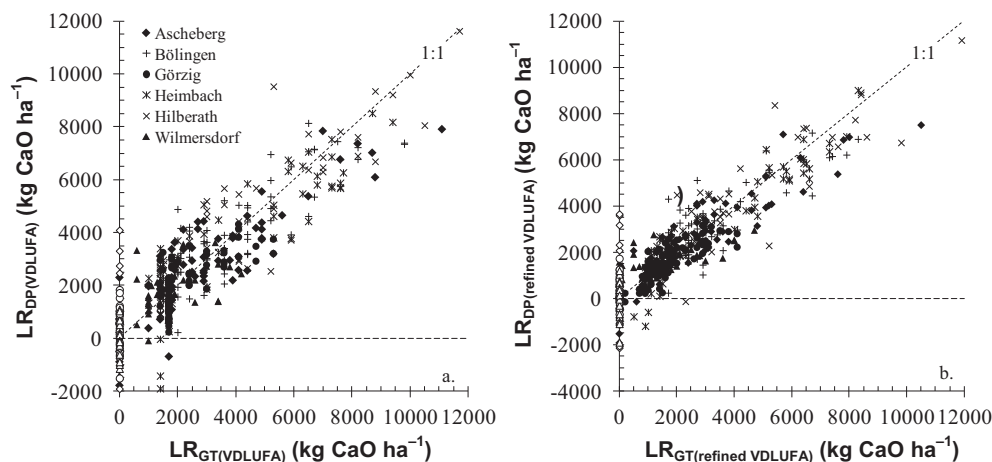
The statistical assessment of  $LR_{DP}$  revealed a performance almost equivalent to  $LR_{SPP}$  (Tab. 4). For all locations except Gö,  $R^2$  and *RMSE* were slightly worse compared to  $LR_{SPP}$ . In total, *RMSE* of the  $LR_{DP}$  approach ranged from 811 to 1420 kg CaO ha<sup>-1</sup>. These errors seem important, but the range of  $LR_{GT}$  is significantly higher and ranged, e.g., at As from 0 kg CaO ha<sup>-1</sup> to more than 11000 kg CaO ha<sup>-1</sup>. The *RPD* for Gö, Wi, and Hi still indicated fair predictions. For As and Bö, good models, and for He even very good models were calibrated. Test-set validation carried out at the locations with  $n > 70$  was also successful and achieved even better results [*RPD* = 2.02 (As), 2.23 (Bö), and 1.61 (Gö), respectively; results not shown]. Again, replacing the look-up table by the refined algorithm further enhanced performance of LR prediction (Fig. 4a, b, Tab. 4).

Our well performing direct LR predictions were in good agreement with studies by Janik et al. (1998) and Viscarra Rossel et al. (2006). However, these two studies investigated Australian soils with mineralogical and pedological properties largely deviating from the soils studied here. In addition, the reference methods to determine GT were different. While Janik et al. (1998) used the 14-day equilibration approach by Richards (1992), Viscarra Rossel et al. (2006) applied the buffer method (Mehlich, 1976). The problem of erroneous LR estimation in calcareous samples as described above was not addressed in both studies.

**Table 4:** Model parameters for the determination of lime requirement (LR) following four different MIRS based approaches:  $LR_{SPP}$ : single parameter predictions of soil properties and subsequent LR determination using the original VDLUFA look-up tables with classified SOM and clay content;  $LR_{SPP}$  (refined VDLUFA): like  $LR_{SPP}$  but using a refined VDLUFA algorithm based on continuous SOM and clay values; direct prediction of lime requirement ( $LR_{DP}$ ) after with standard VDLUFA LR; direct prediction of lime requirement ( $LR_{DP}$ ), but with the refined VDLUFA algorithm ( $R^2$ : coefficient of determination; *RMSE*: root mean square error; *RMSECV*: root mean square error of cross validation; *RPD*: ratio of performance to deviation).

Location	<i>n</i>	$LR_{SPP}$ (VDLUFA) (kg CaO ha <sup>-1</sup> )		$LR_{SPP}$ (refined VDLUFA) (kg CaO ha <sup>-1</sup> )		$LR_{DP}$ (VDLUFA) (kg CaO ha <sup>-1</sup> )			$LR_{DP}$ (refined VDLUFA) (kg CaO ha <sup>-1</sup> )		
		$R^2$	<i>RMSE</i>	$R^2$	<i>RMSE</i>	$R^2$	<i>RMSECV</i>	<i>RPD</i>	$R^2$	<i>RMSECV</i>	<i>RPD</i>
Ascheberg	115	0.82	987	0.87	781	0.72	1220	1.89	0.76	1051	2.04
Bölingen	71	0.75	1030	0.75	832	0.71	1090	1.87	0.69	925	1.79
Görzig	112	0.54	832	0.71	525	0.55	811	1.48	0.66	561	1.72
Heimbach	62	0.86	970	0.92	645	0.77	1230	2.08	0.87	824	2.78
Hilberath	39	0.70	1414	0.78	1197	0.68	1420	1.77	0.74	1260	1.96
Wilmsdorf	59	0.61	857	0.68	716	0.52	905	1.44	0.47	903	1.38





**Figure 4:** Lime requirement (LR) as directly predicted *via* mid-infrared spectroscopy ( $LR_{DP}$ ) compared to LR derived from ground truth ( $LR_{GT}$ ) (a) using the standard VDLUFA algorithm with soil organic matter and clay content classes and (b) using a refined, *i.e.*, stepless VDLUFA. Underlying  $LR_{DP}$  models were calibrated for each location by leave-one-out cross validation. Empty symbols represent calcareous samples from Ascheberg, Görzig, and Wilmersdorf.

### 3.4.1 Erroneous LR prediction for calcareous samples in the $LR_{DP}$ approach

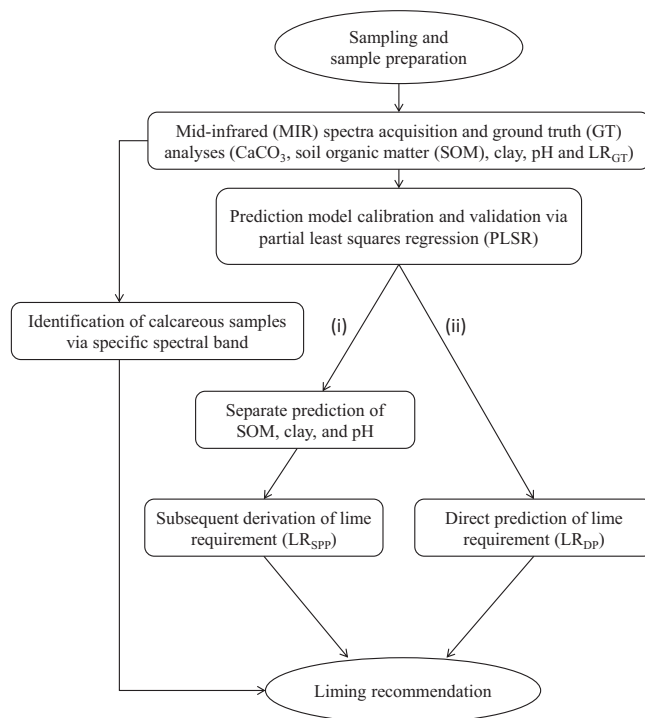
Direct prediction was conducted without precedent spectral carbonate identification. For a number of calcareous samples,  $LR_{DP}$  led to erroneous liming recommendation (−2000 to 4000 kg CaO ha<sup>−1</sup>; Fig. 4b). Predicted negative LR can subsequently be corrected to zero. In particular, a false-positive LR was determined for calcareous samples with high target pH (*i.e.*, clayey samples) and actual pH < 7 (*i.e.*, samples with remaining undissolved lime particles) as already described above.

To unravel the causes for the obvious under-representation of carbonate in model calibration, we examined the loading weights of the first latent variables. It turns out that the carbonate-specific bands were only of minor importance for calibrating  $LR_{DP}$  (results not shown). As a consequence, the  $LR_{DP}$  was inappropriate for differentiation between calcareous and non-calcareous samples. Thus, we recommend identifying calcareous samples by peak height at 2513 cm<sup>−1</sup> and the subsequent exclusion of the related field sites from liming.

LR integrates several soil properties that depend on regional (*e.g.*, climatic) conditions; for practical purposes, LR is adapted to agronomic needs. Successful LR prediction reflects the capability of MIRS to quantify the underlying soil properties such as content and molecular composition of organic matter (reflecting CEC as well as pH value), as well as textural and mineral soil composition (content and properties of clay, iron oxides, and other minerals). In this regard, the MIRS based prediction models go far beyond the look-up-table approach. It can be concluded that MIRS generally improves LR determination as compared to the common practice. With MIRS suitable information for variable rate liming within the fields can be acquired.

## 4 Conclusions

This study showed that MIRS is an appropriate tool for variable rate liming recommendation based on the standard German VDLUFA algorithm. Both tested approaches, the determination of lime requirement from precedent separate parameter prediction ( $LR_{SPP}$ ) and the direct prediction of lime requirement ( $LR_{DP}$ ; Fig. 5) yielded reliable and accurate



**Figure 5:** Recommended process flow for determination of lime requirement (LR) *via* mid-infrared spectroscopy (MIRS) for precision farming applications including two alternative approaches: (i) derivation from single parameter (SOM, clay, and pH) predictions ( $LR_{SPP}$ ) and (ii) direct prediction ( $LR_{DP}$ ).

results. The performance of LR<sub>DP</sub> is slightly less accurate while LR<sub>SPP</sub> is more complex. In both approaches the identification of calcareous samples via the carbonate specific band at 2513 cm<sup>-1</sup> is recommended, because false-positive liming recommendations contradict the basic idea of precision agriculture. Concluding, MIRS as an easy, rapid and cheap approach can contribute to a broader and site-specific evaluation of LR in agricultural practice. This is notably true for precision farming applications, where large sample numbers from field plots are to be analyzed.

As an extension of the standard German VDLUFA algorithm, MIRS has the potential to refine the existing recommendation tables by introducing a continuous algorithm. This approach would easily increase the efficiency of variable rate liming. Instead of mixing all soil samples from a field to create a composite sample, for variable rate liming georeferenced single samples within identified management zones have to be taken. This approach is worth being tested with the upcoming mobile MIRS devices.

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