

IMPROVEMENT OF THE QUALITY OF “ON-THE-GO” RECORDED SOIL PH

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ABSTRACT

The recording of soil pH is an important basis for lime fertilisation. Many studies have shown that soil pH can vary greatly on a small-scale. With the development of a sensor from the company Veris (Kansas, USA) it has become possible to determine the soil pH in a much higher sampling density relatively cheaply compared to the time and cost intensive laboratory method. The two methods differ fundamentally with respect to their measurement principles as an extraction medium is used in the laboratory method. This means that the difference of the results between the methods increases with falling pH value and recalibration of the sensor values is necessary (ROWELL, 1997).

Statements about the agreement and precision of both methods using studies of identical soil samples form the subject of this paper. As a last point, a recommendation will be shown for calibration of the sensor values, which makes practical use of the sensor possible.

In the literature, mainly the correlation coefficient r or R^2 is given as quality criteria for the agreement of the results of both methods in studies with the equivalent sensor. This is, however, unsuitable for a comparison of methods, since it reproduces only the relation between two measurement sizes. The Mean Absolute Error (MAE) and the Root Mean Square Error (RMSE) is suitable for the measurement of agreement. The results of the repeated sampling for the laboratory method show only a medium quality for the repeated precision of ($R^2=0.71$; MAE=0.25; RMSE=0.46). The results of the comparison of the raw data of the sensor with the laboratory method are unacceptable ($R^2=0.86$; MAE=0.77; RMSE=0.83). The error can only be reduced to an acceptable level (MAE=0.22; RMSE=0.30) through a post-calibration with the developed algorithm. Further statistical tests support the suggested calibration. The approach developed was able to be tested on several practice fields and could be used as the basis for sub-field specific liming.

Keywords: Veris-MSP, soil pH, accuracy, site-specific lime application

INTRODUCTION

With the introduction of precision farming technology the goal followed is that of using plant cultivation methods sub-field specifically. A high density of information is necessary for this in order to enable cultivation to be carried out as needed. Fertilisation with a uniform application inevitably leads to zones with over- or under-fertilisation on fields, which has negative ecological and economic consequences.

In a joint project between the Martin-Luther-University Halle-Wittenberg and the precision farming company Agri Con (Saxony, Germany) the potential of sub-field specific lime application is investigated with the Veris – Mobile Sensor Platform (MSP) pH- Manager (Kansas, USA). It is possible to measure the soil pH whilst driving over the field with the sensor and obtain the sampling density in a much higher resolution than with the usual sampling methods. Publications up to now, in which the Veris sensor has been tested, evaluated or used as the basis for sub-field specific liming describe the importance of a field specific calibration and refer to the measurement discrepancy between the laboratory and sensor methods. This difference can be traced back to the use of an extraction solution which releases the latent bound H^+ ions (ROWELL, 1997). The knowledge of the soil pH determined through the laboratory method is necessary, however, since the decision rules of lime fertilisation are based on this. Further influencing factors for the fertilisation recommendation are the soil texture and the content of organic matter (VDLUFA, 1991).

This article introduces an approach that minimises the discrepancy to the laboratory method through a post-calibration of the raw data. For this, the precision of both measurement methods are presented and the approach for post-calibration demonstrated and evaluated. Finally, the approach is used under field conditions with a view to its practicability.

LITERATURE

BIANCHINI and MALLARINO (2002) show that the soil pH can vary by 2 units within an interval of 12 m. They thus illustrate that a small-scale recording of the soil pH with relatively cheap methods, such as with sensor technology, has a high potential. Further studies confirm that the soil pH can differ greatly in a small area (FU et al., 2010, LAUZON et al., 2005). CONYERS and DAVEY (1990) determine that ca. 30 to 100 % of the variability of the soil pH can occur within about 1 m². On a micro-scale level with oil-seed rape seedlings, MURANYI et al. (1994) show that the soil pH can vary by 1.7 pH units in an interval of less than a few millimetres from the roots.

The Veris-MSP has been investigated in several studies. The main questions relate to the direct comparison of the results from the Veris-MSP and the laboratory method or a direct comparison of the resulting maps from the different ap-

2010									
Schirrmann et al., 2011	identical		x	x	x	x		inverse regression	x
	non-identical (< 1m)	x	x	x	x	x			x
Staggenborg et al., 2007	non-identical (< 1m)		x	x			x	t-test	x

using the same extraction solution. However, the two methods do not analyse identical soil samples. For the comparison of the results according to both methods, the results are interpolated onto a uniform raster of 2 x 2 m. The following evaluation of the sensor is made using the interpolated map with the coefficient of determination, the RMSE for precision, the mean error for the bias and the standard deviation of the error for precision. Large deviations occurred mainly with the use of de-ionised water with a RMSE of 0.68, ME of 0.66 and R² of 0.67. A better agreement could be determined through the use of calcium chloride (RMSE = 0.37; ME = 0.30 and R² = 0.64). It also shows that the sensor displays a lower pH range than the laboratory method.

For a comparison of methods BLAND and ALTMAN (1986) as well as SACHS (1990) point out that the evaluation of the agreement through the coefficient of determination or the correlation coefficients is unsuitable. KOCH and SPÖRL (2007) show that a comparison of methods must be classified into population related and intra-individual problems and must thus differ fundamentally from the statistical approach. Thus, for instance, the concordance-correlation coefficient from LIN (1989) is better suited than the Pearson correlation coefficient.

MATERIALS AND METHODS

Methods of pH determination

The determination of the soil pH with the Veris-MSP differs clearly from the stipulated laboratory method. Soil removal occurs through a single probe from a soil layer of ca. 8 to 15 cm. The soil sample is pressed against the two pH sensitive antimony electrodes and the pH value is determined in a measurement time of ca. 10 to 15 seconds. The electrodes are then rinsed and are ready for the next measurement. Before each field sampling, the electrodes are calibrated with two buffer solutions with pH values of 4 and 7.

For the soil pH analysis using the laboratory method (for a representative homogeneous field of 1 to 5 ha) a mixed sample should be taken from 20 to 30 individual probes from the cultivated soil depth (0 – 30 cm) (VON WULFFEN et al., 2009). The sample is prepared in the laboratory by drying, sieving to 2 mm and mixing with 0.01 mol l⁻¹ calcium chloride solution in a ratio of 1 : 2.5. After one hour reaction time and stirring twice, the analysis of the pH value is made using a pH measuring device (VDLUFA, 1991).

One aim of this article is to make statements about the precision of both methods for the determination of the pH value of soil samples. In order to exclude the influence of a possible pH gradient and micro-variability, identical soil samples were always analysed for both analysis techniques.

Statistical approach for comparing methods

LIN (1989) shows the weaknesses of the Pearson's correlation coefficient in a method comparison and defines the concordance correlation coefficient according to the following equation:

$$r_{ccc} = \frac{2 * S_{xy}}{S_x^2 + S_y^2 + (\bar{\mu}_x - \bar{\mu}_y)^2} \quad (1)$$

where $S_x^2; S_y^2$ are the sums of the average squared deviation from the mean ($\bar{\mu}_x; \bar{\mu}_y$) and S_{xy} is the covariance.

The equation for the calculation of r_{ccc} takes into account (through a penalty term) the deviation from the line of equality. The Pearson's correlation coefficient (r) does not record this sort of deviation. If there are no deviations from the best fit line then r and r_{ccc} take the same value.

A direct evaluation of the agreement of the methods can be carried out with the error measurement mean error (ME), mean absolute error (MAE) and root mean square error (RMSE). With the ME, the deviations are measured independently from the signs (positive or negative), whilst the MAE measures the absolute deviation. Due to its formula, the RMSE weights outliers higher than small deviations. The nearer the error measurement comes to 0, the lower are the deviations.

BLAND and ALTMAN (1986) suggest a simple, graphical analysis with which trends and outliers can be detected for the discrepancy of the results of the investigation into precision of reproducibility. The prerequisite for this is that two measurement results are known for a soil sample. The difference of both results is plotted on the ordinate (y axis) and the mean of both results on the abscissa (x axis). A t-test can be used to verify if the mean difference is different from zero. Finally, a statistical tolerance area is given, which should be smaller than the technically permitted tolerance area.

For a method comparison PASSING and BABLOK (1983) show that a regression using the method of the least squares is unsuitable. The preconditions, e.g. no measurement error of the validated method, are often violated. They suggest a robust regression, which is implemented by SAS (2008).

Calibration with selected soil samples

Through results of studies of other authors and our own studies, the need for a field-specific calibration of the raw data of the Veris sensor to the results of the laboratory method is known. The approach for calibration must be practical here, but also enable a precise and correct fit. The suggested calibration approach is based on selected soil samples. After the normal soil sampling with the Veris sen-

sor, the results are shown in a GIS programme and the measurement points are ordered according to increasing pH values. The selection of suitable calibration probes occurs by taking into account that an even distribution of measurement points is available throughout the whole pH measurement area. A difference of 0.2 pH units between the measurement points is aimed for here. Table 2 shows an example for the selection of samples.

Table 2. Example for selecting post-calibrated samples.

Number	Longitude	Latitude	pH (electrode 1)	pH (electrode 2)	pH (avg. of both el.)	Select
n	degree	degree	pH	pH	pH	yes/no
1	12.4607249	50.8210245	5.31	5.39	5.35	Y
2	12.4569525	50.8202747	5.37	5.43	5.40	N
3	12.4555107	50.8208609	5.49	5.61	5.55	Y
4	12.4536487	50.8206537	5.50	5.70	5.60	N
5	12.4517037	50.8201557	5.73	5.65	5.69	N
6	12.4504712	50.8197827	5.80	5.68	5.74	Y
...						
725	12.4505605	50.8188574	7.30	7.45	7.375	N
726	12.4516208	50.8190354	7.32	7.48	7.40	Y

This thus creates the basis for the post-calibration. In a second drive over the field, the selected measurement points are sampled a second time with the Veris-MSP with the difference that the sample is moved to the measurement sensor manually. After the measurement has been carried out, the soil sample is put in a bag and analysed using the laboratory method. In this way it is ensured that the Veris-MSP and the laboratory analyse **identical** sample material and that influences caused by small-scale variability and a possible pH gradient can be excluded. On the one hand, statistical improvements are evaluated, and, on the other hand, economic working aspects.

Data basis

For the investigation into the reproducibility of both methods, samples from different locations were analysed twice ($n_{\text{Sensor}} = 63$, $n_{\text{Laboratory}} = 154$). The comparison between the methods was carried out in a long-term lime fertilization experiment of the Martin-Luther-University Halle. The location is characterised by loamy sand, 494 mm average annual precipitation and 9.2 °C average annual temperature. In four steps from 0, 0.5, 1 and 2 t CaO ha⁻¹, carbonic lime is applied

every three years after the cereal harvest. 66 soil samples were available for the investigation. The evaluation of the suggested calibration approach is presented and carried out in this study. Identical sample material was always used for the trials for reproducibility of each method and for precision of both methods to one another. In the second part the results of sampling with the Veris-MSP under field conditions are presented and discussed.

RESULTS AND DISCUSSION

Precision within and between the methods

Both methods obtain good results in the repeated measurements with slight advantages for the method of the Veris-MSP (see table 3). Noticeable, are the differences between both methods. The results from the Veris-MSP show a clear over-estimation of the soil pH compared to the laboratory method. The concordance-correlation coefficient, with a value of 0.57, is only modest, compared to the repeated measurements. Also, the slight difference of the two parameters ME and MSE shows that nearly all measurement values were over-estimated by the Veris-MSP.

Table 3. Results of method comparison between Veris-MSP and laboratory and within methods.

method of measurement	laboratory		Veris-MSP		laboratory vs. sensor	
	t=1*	t=2*	t=1*	t=2*	sensor	lab.
statistical data						
n	154		63		66	
pH _{min}	5.20	5.20	6.20	6.20	5.78	4.66
pH _{mean}	6.09	6.12	7.13	7.23	6.95	6.19
pH _{max}	7.50	7.40	8.10	8.20	8.14	7.33
STDV	0.81	0.82	0.55	0.57	0.61	0.80
r _{PEARSON}	0.84		0.93		0.93	
r _{CCC}	0.84		0.92		0.57	
ME	-0.03		0.10		0.77	
MAE	0.25		0.17		0.77	
RMSE	0.46		0.23		0.83	

* time of measurement

Through similar results ADAMCHUK et al. (2011), SCHIRRMANN et al. (2011), and JONJAK (2011) come to the conclusion that the raw data of the sensor has to be calibrated. On the other hand, it is clear from the magnitude of the errors, that the tried and tested laboratory method is afflicted by a larger error level. In the introduction of a new measurement method for the pH value, SCHIRRMANN et al. (2011) define the goal that a maximum deviation of +/-0.05 pH units from the reliable laboratory method should not be exceeded. With a MAE of 0.25 pH units,

the laboratory method shows, however, that it does not fulfil this requirement itself. For the lime application, this sort of deviation could result in over-fertilised liming of up to 2.4 t CaO ha⁻¹ (ca. 70 € ha⁻¹)¹. Additionally, the aspect of the small “representative” sampling density of 0.2 ha⁻¹ to max. 1 ha⁻¹ should not be forgotten.

The plots (set out using the recommendation by BLAND and ALTMAN, 1986) illustrate the greater distribution of the laboratory method compared to the sensor method (see figure 1). For both measurement methods the regressions coefficient *b* is not significantly different from zero for the differences related to the mean of the individual pairs (for the sensor: *b* = -0.02, *p*-value = 0.69; for the laboratory: *b* = 0.00, *p*-value = 0.90).

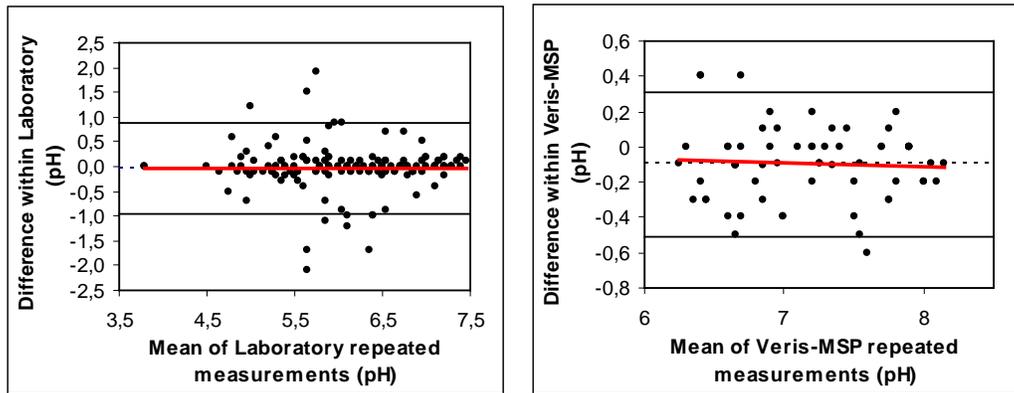


Fig. 1. Bland-Altman plots of the laboratory and Veris-MSP measurement methods (red line: regression line of the difference compared to the average dashed line; average of the differences, thin continuous line: tolerance area of the differences with MW ± 1.96 * standard deviation of the differences).

This shows that no trend is measurable with either method with increasing or decreasing soil pH. The statistical tolerance area lies in a region of -0.51 to $+0.32$ pH units for the Veris-MSP. A larger tolerance area of -0.94 to $+0.88$ pH units arises for the laboratory method.

The comparison between both methods shows that a significant trend can be determined for the differences ($b = -0.29$, $p < 0.001$). The differences decrease with increasing soil pH. The average difference is equal to $+0.75$ and thus underlines the strong deviation (see figure 2).

It is clear from table 3 that the tried and tested laboratory method is error prone and thus violates the preconditions of the regression using the method of the least squares. Other regression approaches are suitable for this sort of problem, such as the suggested method from PASSING and BABLOK (1983). Additionally, it follows from the table that the correlation coefficient should serve as a complementary criterion, not as the main one for the agreement. The dependence of the correlation coefficient (according to Pearson and Lin) on the range is questionable any-

¹ Calculation assumption: soil group: 5; 0.3 pH-difference equivalent to 2.4 t CaO ha⁻¹ difference; price per t CaO: 29 €; 2.4 t CaO ha⁻¹ x 29 € t⁻¹ CaO⁻¹ = **69.6 € ha⁻¹**

way. With a consistent distribution of the independent variables throughout the range, there would be a better agreement with a wider range of the independent variables through a presumably higher correlation coefficient. This is, however, incorrect. In an evaluation of two methods, which measure an identical target value, several statistical methods must be used in order to avoid incorrect interpretation or incorrect statements.

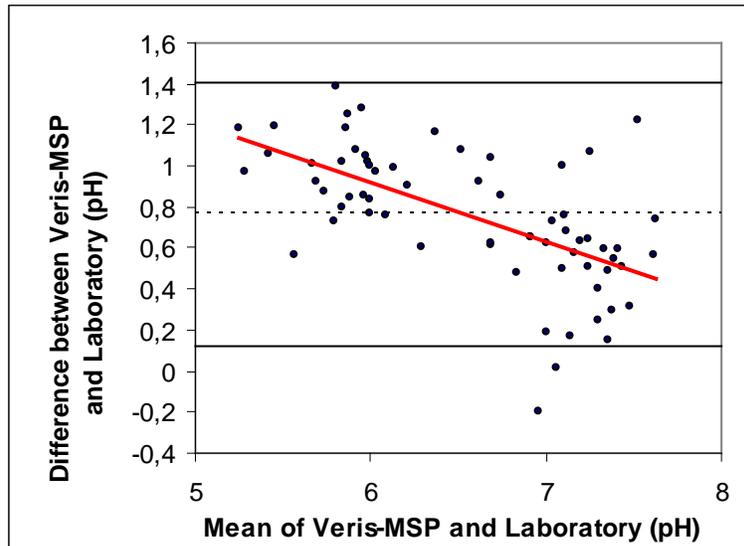


Fig. 2. Bland-Altman plot between both methods

Calibration with selected soil samples

The calibration recommendation is demonstrated and evaluated firstly using the example of the long-term line fertilisation trial. According to the regression analysis by PASSING and BABLOK (1983) the following regression line is given:

$$pH_{calibrated} = 1.25 * pH_{Veris} - 2.541 \quad (2)$$

The suggested approach for calibration leads to a clear lowering of the magnitude of error by more than 0.5 pH units (see table 4). The Pearson's correlation coefficient remains undisturbed in a functional transformation so that no change can be expected here. A much better improvement is shown by the concordance correlation coefficient, which approaches the value of the Pearson's coefficient.

Table 4. Evaluation of approach for calibration of Veris-MSP data

method of measurement	Laboratory	Veris MSP	
		raw data	calibrated data
n		66	
pH _{min}	4.66	5.78	4.67
pH _{mean}	6.19	6.95	6.14

pH _{max}	7.33	8.14	7.62
STDV	0.80	0.61	0.77
r_{PEARSON}		0.93	0.93
r_{CCC}		0.57	0.93
ME		0.77	-0.05
MAE		0.77	0.22
RMSE		0.83	0.30

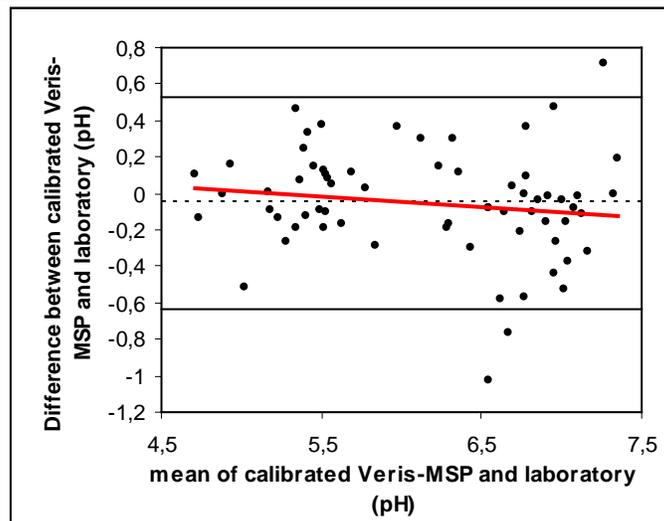


Fig. 3. Bland-Altman plot of the calibrated sensor values and laboratory values.

With the calibration the significant negative trend of the discrepancies with increasing soil pH could be eliminated. The regression coefficient after the calibration is -0.06 with a p-value of 0.21 (see figure 3). The calibration takes extra time and expense, but clearly improves the quality of the sensor data.

Other suggestions for calibration in identical (SCHIRRMANN et al., 2011) and non-identical soil samples (ADAMCHUK et al., 2011; ADAMCHUK et al., 2007; JONJAK, 2011) lead to different improvements.

The discrepancy between the measurement results of the laboratory method and the Veris-sensor is confirmed and discussed by other authors (SCHIRRMANN et al., 2011; JONJAK, 2011; OLFS et al., 2010). Explanatory approaches revert mainly to the use of extraction medium in the laboratory method (ROWELL, 1997; SCHIRRMANN et al., 2011; OLFS et al., 2010). Not to be excluded is also a possible pH gradient, when the comparison of soil samples comes from different soil layers (STAGGENBORG et al., 2007; LUND et al. 2004).

Use of the Veris-MSP under field conditions

The practice field „Lange Winde“ was sampled using the Veris-MSP in the summer of 2011 as part of a trial series. Before the sampling, no information was available about the possible heterogeneity, in particular about the soil pH.

654 measurements were carried out on a trial field of 45 ha, of which 37 measurements (6 %) had to be excluded due to measurement errors (electrode differ-

ence larger than 0.5 pH units). For the use of the suggested calibration approach 25 soil samples were measured manually using the Veris-MSP for the calibration and validation in the second sampling drive; afterwards the identical material was analysed using the laboratory method. The most important results of the sampling, calibration and evaluation are summarised in table 5. It becomes clear that the calibration approach also leads to very good improvements under field conditions. The magnitude of error could be much improved and allow the calibrated data to be used.

Table 5. Results of calibration from trial site.

used data for calibration	raw data	calibrated*
size (ha)		45
no. of Veris-MSP samples		617
no. of lab samples		25
used lab samples for calibration	none	13
used lab samples for evaluation		25
pH _{min}	5.65	4.69
pH _{mean}	7.21	6.46
pH _{max}	7.99	7.35
STDV	0.48	0.55
r _{PEARSON}	0.98	0.98
r _{CCC}	0.66	0.98
ME	0.83	0.00
MAE	0.83	0.14
RMSE	0.84	0.17

* regression function: $\text{pH}_{\text{calibrated}} = 1.133 \times \text{pH}_{\text{Veris}} - 1.712$

Figure 4 shows the spatial distribution of the soil pH. Noticeable here is the small-scale pH differentiation, which could be repeatedly measured through neighbouring sampling tracks. Differences of up to 2.3 pH units were found within less than 65 m (marked in black box in figure 4).

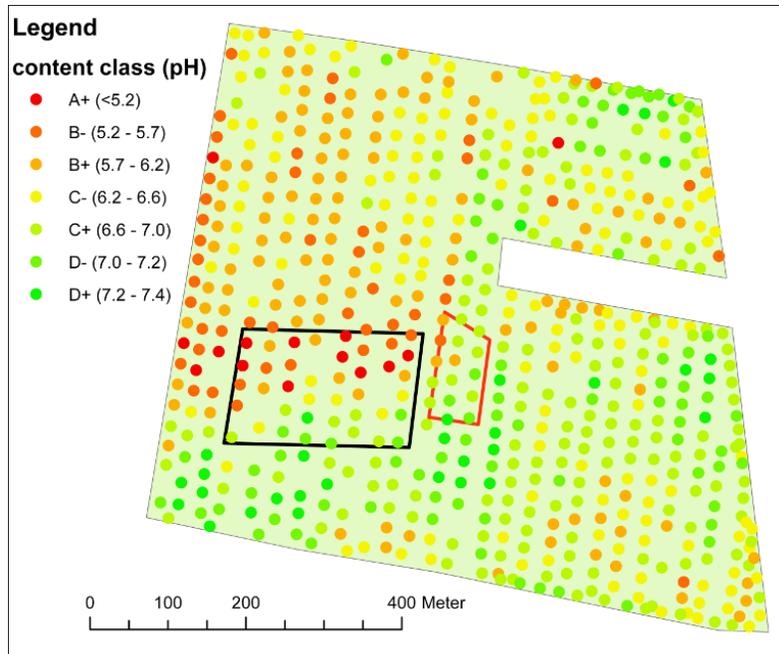


Fig. 4. Spatial pH-value distribution „Lange Winde“.

During sampling with the Veris sensor, the recording software visualises the measurement results. For a section (marked in red in fig. 4) large differences in soil pH were found in a very small area, which meant that an intensive sampling was carried out. The results of the small-scale sampling are shown in figure 5. On an area of 0.64 ha, 46 probes were measured, which equates to a sampling density of 72 probes ha⁻¹. The soil pH varies between 5.9 and 7.4.

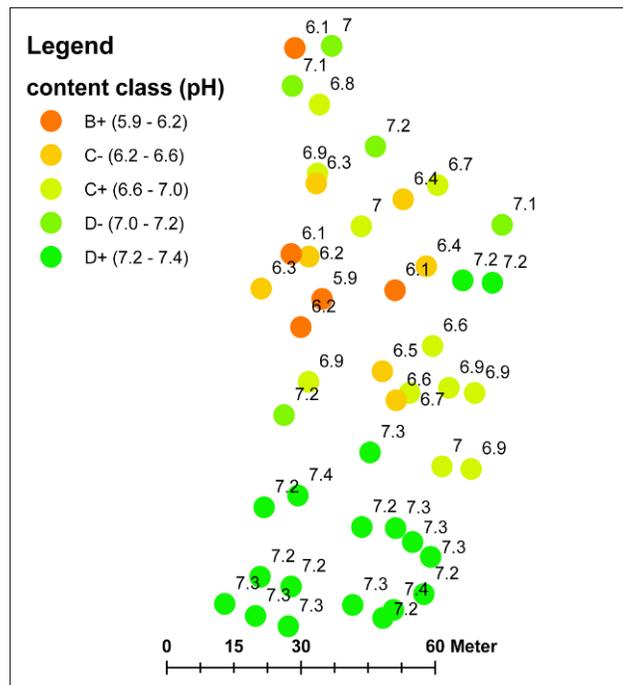


Fig. 5. Small-scale pH variability.

Very good small-scale pH variability could be repeatedly measured with the sensor. A comparably high resolution soil sampling with normal methods fails due to the high laboratory costs on the one hand, and due to the lack of knowledge about the heterogeneity of the soil pH on the other hand.

The required total working time for the sampling amounted to 4 hours and 45 minutes. This estimates 30 minutes for the preparation and follow-up work to get the sensor ready, 3 hours for the sampling and 75 minutes for calibration with the approach presented here. Extra costs arise of 2 € per sample for calibration costs. This means that the total costs² for the calibration are estimated at ca. 4 € ha⁻¹ in addition to the costs for the normal sampling.

CONCLUSION

The implementation of sub-field specific liming requires a high density of information. The reasons for this are, on the one hand, a possible small-scale variability of the soil pH and on the other hand, a lack of instruments for high resolution, cheap sampling. With the usual sampling, a high density of probes of more than 1 probe per ha⁻¹ is not economically feasible due to labour and laboratory costs. Veris-MSP offers an alternative with its pH sensitive measurement technique. Results from other authors and our own investigations of identical soil samples using both methods allow the conclusion to be made that it is necessary to fit the measured pH values from the Veris-MSP to the laboratory results. With the suggested approach for calibration it could be shown that the difference between both methods could be much minimised under experimental and practical conditions. Small-scale variations can be recorded in probe densities of more than 10 probes ha⁻¹. The extra expenditure is estimated at ca. 4 € ha⁻¹. This higher cost appears to be justifiable due to the extra information obtained.

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² 1.25 h x 100 € h⁻¹ + 50 samples x 2 € sample⁻¹ = 175 € : 45 ha = **3.89 € per hectare**.

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