# On-the-go tropical soil sensing for pH determination using ion-selective electrodes

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Abstract – The objective of this work was to assess the performance of an antimony ion-selective electrode (ISE) sensor system, using manual and automatic operating modes, for measuring the potential of hydrogen (pH), in real time, in Oxisols with different characteristics. Samples were manually collected and sent to a laboratory for determination of pH in water and calcium chloride, whose values were used as references. Another set of samples was also automatically collected using a commercial equipment, and readings were performed in manual mode. The performance parameters of the sensor system were calculated and evaluated. Part of the soil samples was used to assess the degree of influence of moisture in determining pH. Calibration lines were constructed. The statistical analysis revealed better results for the manual mode. Both modes of operation had errors superior to those accepted as a limit in laboratory techniques, however, with the possibility of high data density and with positive and promising results. Soil moisture interfered with the result of the readings. The sensor system yields a sampling density of 45 data per hectare, which represents a great contribution to the intensification of data for a better spatial evaluation of soil information.

Index terms: direct soil sensing, precision agriculture, real-time mapping.

# Mensuração direta do pH de solos tropicais por meio de eletrodos íon seletivos

Resumo – O objetivo deste trabalho foi avaliar o desempenho de um conjunto sensor direto, de íon seletivo (ISE) de antimônio, usando os modos de funcionamento manual e automático, na determinação do potencial hidrogeniônico (pH), em tempo real, em Latossolos com diferentes características. Amostras foram coletadas com trado e encaminhadas a laboratório para a determinação do pH em água e do cloreto de cálcio, cujos valores foram utilizados como referência. Um segundo conjunto de amostras foi coletado automaticamente utilizando-se um equipamento disponível no mercado, e foram executadas leituras em seu modo manual. Parâmetros de desempenho do conjunto foram calculados e avaliados. Parte dessas amostras de solo foi utilizada para avaliar a influência da umidade na determinação do pH. Retas de calibração foram construídas. As análises estatísticas apresentaram melhor resultado para o modo manual. Ambos os modos de operação apresentaram erros superiores aos aceitos como limite em técnicas laboratoriais, porém, com a possibilidade de elevada densidade de dados e com resultados positivos e promissores. Verificou-se que a umidade do solo interferiu no resultado das leituras. O conjunto sensor fornece uma densidade de amostragem de 45 dados por hectare, o que representa uma grande contribuição para a intensificação de dados para melhor avaliação espacial da informação do solo.

Termos para indexação: sensores diretos de solo, agricultura de precisão, mapeamento em tempo real.

## Introduction

Soil physical, chemical, and biological properties are directly or indirectly associated to its acidity, considered as a limiting factor of crop yield. In tropical regions, soil acidity problems are detected below the pH range between 5.0 and 6.0, required for the majority of crops. Problems caused by soil acidity include nutritional deficiency and toxicity, and low water-holding capacity and microbial activity, which prevent high crop yields.

Approximately 70% of the agricultural land in Brazil is composed of soils that are acidic, contain toxic levels of $Al^{3+}$ and $Mn^{2+}$ and exhibit low base saturation (Soratto & Crusciol, 2008). These soils primarily contain kaolinite and iron and aluminium sesquioxides; and these minerals have variable charges and are highly influenced by the potential of hydrogen

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(pH) of the medium. Based on potential acidity, liming is a process that is commonly employed to neutralise acidity, improve the root environment and restore the productive capacity of soils (Caires et al., 2008).

As for the other physical and chemical soil attributes, pH values can vary within a field, which justifies the application of limestone according to the spatial variation of soil pH (Gebbers et al., 2010). Nonetheless, available sampling strategies are feasible with densities of 1 sample per hectare or less, because of cost limitations (Khosla et al., 2010). Grid sampling with distances larger than 100 m between samples are not sufficient for representing soil pH variability in the field (Brouder et al., 2005). As a result, pH, CEC, and base saturation (BS) attributes, considered for lime demand calculation, must be accurately mapped, which is primarily influenced by sampling density (Gebbers et al., 2009).

A prototype for determination of the hydrogen potential (pH) in real time was developed and tested by Adamchuk et al. (1999). Its sampling mechanism consisted of a horizontal collector, mounted to the three-point hitch on a farm tractor, working at an average depth of 0.1 m and with subsequent contact with a pair of electrodes. The field maps obtained through this practice had their results compared to those of a set of soil samples manually collected and analyzed by a commercial laboratory, demonstrating potential application in agriculture. The automated collection of soil pH data showed that the higher resolution provided by these data can reduce errors, resulting in potential for use in recommendations for application of lime at variable rates. Other automated systems for direct measurement of soil pH were proposed, developed and tested under field conditions, like the one by Collins et al. (2003), with positive results, which motivates the continued investment on this approach.

An economical analysis of soil pH mapping with a commercial sensor system, derived from the one described by Adamchuk et al. (1999), was tested in Nebraska, USA, and resulted in net income increase of US$ 6.13 ha$^{-1}$ for lime application in a simulation of four years of a corn-soybean rotation and with lower errors, even with relatively lower accuracy in individual measurements (Adamchuk et al., 2004). Estimation of lime requirements, in Australia, based on conventional and sensor based pH measurement, using that same commercial system, resulted in error of 0.6 Mg ha$^{-1}$ (Viscarra Rossel, et al., 2005). The same system was tested on different edafoclimatic conditions, on eight fields, in six USA states, for two years. Those tests contributed to show the potential use of lime variable rate recommendations based on high-density data from automated systems (Adamchuk et al., 2007).

Positive results for measuring soil pH in real time with high sampling density may improve the speed and efficiency of sampling and analysis, and represent an important solution for agriculture demands.

The objective of this work was to assess the performance of an antimony ion-selective electrode (ISE) sensor system, using manual and automatic operating modes, for measuring the potential of hydrogen (pH), in real time, in Oxisols with different characteristics.

## Materials and Methods

The study was performed in recently established areas that had been cultivated with sugarcane. The experimental areas were located in an area in the municipality of Piracicaba, in the state of São Paulo, Brazil. The study was performed in three areas with soils belonging to the Oxisol order, varying on clay content (sandy loam and clayey texture) and base saturation from low (dystrophic) to high (eutrophic), as shown on Table 1. The focus was placed on those conditions to assess interference from the soil attributes, particularly texture, in the real-time determination of pH using ISE, considering that Oxisols are characteristic of tropical regions. They represent one of the most common soil orders in Brazil, covering large agricultural and natural areas (Fontes et al., 2001).

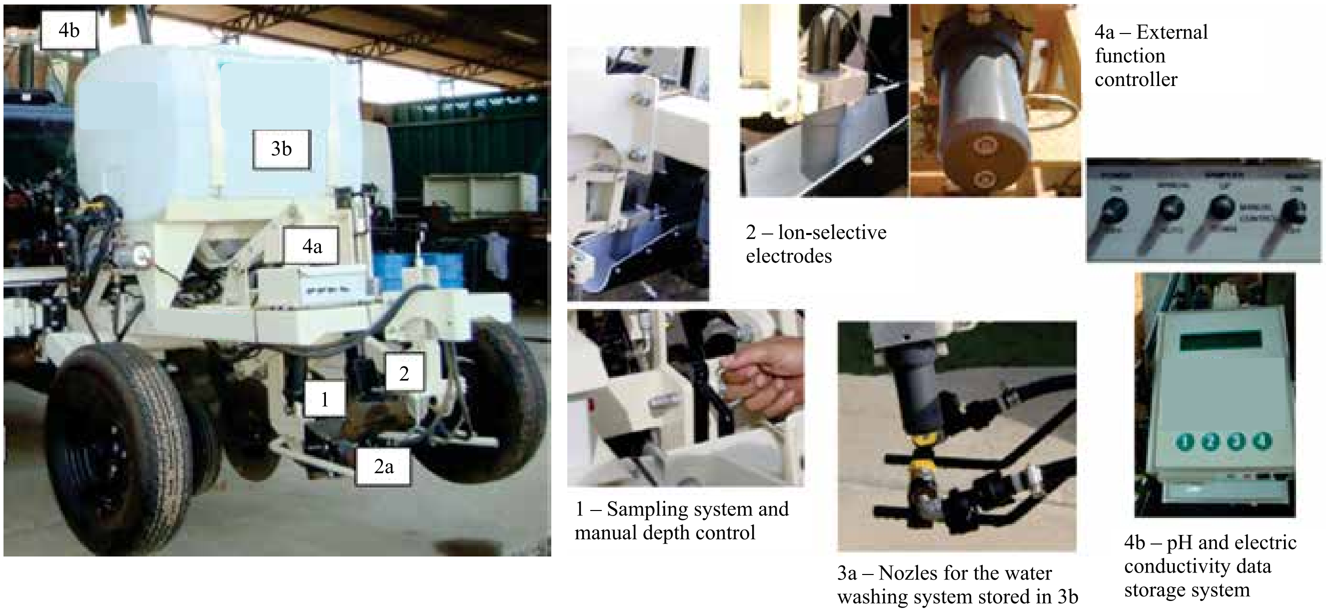
The Mobile Sensor Platform pH (MSP$_{pH}$) (Veris Technologies, Salina, KS, USA) sensor system was employed for on-the-go pH measurements in the field. The sensor system consists of a soil sampler, a water reservoir and potentiometric sensors to measure pH in real time through a pair of antimony electrodes. The potentiometric sensors measure the difference in potential that is generated in the flow of electric current between the electrodes when in contact with a given medium. The metallic antimony electrode that is inserted in a soil solution responds to the concentration of hydrogen atoms, presumably according to the chemical equilibrium of the medium (Joo & Brown, 2008). The system (Figure 1) is attached to the three-point hitch on a farm tractor and operates in a three-stage cycle: i) collection of soil samples using a hydraulically activated probe that is horizontally inserted into the soil with the tractor in motion; ii) lifting of the sampling and pH reading by establishing contact of the soil with the two antimony electrodes; and iii) washing of the electrodes after performing the readings using two water jets to restart the cycle.

The pH reading cycle of the sensor system can be performed in automatic or manual mode. In automatic mode, a horizontal sampling auger collects a sample without intervention of the operator, while the equipment is moved along the field. When the soil contacts the two electrodes, the respective tensions are calculated, and the average pH values for each electrode are recorded after the readings are stabilized; the length of this process ranged from 10 to 30 seconds. The coordinates of the sampling point are simultaneously recorded by a datalogger connected to a Global Navigation Satellite System (GNSS) receiver with satellite differential correction and accuracy under 0.5 m. After measuring the pH, the auger is lowered into the soil again, and the previously collected soil sample is released by the new soil fraction that is introduced into the sampler. The electrodes are simultaneously washed by two washer jets that are installed on each side of the electrode support. The forward speed was approximately 1.5 m $s^{-1}$ and the distance between the passes was 5 m, which produced approximately 60 samples per hectare. The data collection preceded the soil fertility correction procedures.

The manual sampling mode is characterized by the exposition of soil samples to the electrodes simply activating the auger movement with the equipment (tractor and sensor system) under static conditions, only changing samples selected by any criteria. The manual operating mode was employed to quantify the ISE performance by calculating the parameter response time, precision, and accuracy.

**Table 1.** Summary of soil classification for the experimental areas.

| Area | Geographical coordinates | Area (ha) | Classification | Texture | Base saturation (V%) |
|---|---|---|---|---|---|
| 1 | 23°4'22"S; 47°53'52"W | 13.3 | Latossolo Vermelho distrófico (Red Oxisol) | Loamy | <50 (dystrophic) |
| 2 | 23°1'24"S; 47°43'41"W | 11.5 | Latossolo Vermelho eutrófico (Red Oxisol) | Loamy | >50 (eutrophic) |
| 3 | 22°57'59"S; 47°43'10"W | 13.0 | Latossolo Amarelo eutrófico (Yellow Oxisol) | Medium sandy | >50 (eutrophic) |



4a – External function controller

2 – Ion-selective electrodes

1 – Sampling system and manual depth control

3a – Nozles for the water washing system stored in 3b

4b – pH and electric conductivity data storage system

**Figure 1.** Composition of the sensor system that was employed in the study.

Prior to the activation of the sensor system, georeferenced soil sampling was performed. Regular grids of four single samples per hectare were employed. Collection was performed at a depth range of 0–0.1 m with a Dutch auger. Each of the samples were subdivided into four subsamples; and three of the samples were sent to different routine analysis laboratories. In the laboratory, pH of the soil sample was determined after the addition of two different solvents, deionised water and 0.01 N calcium chloride ($CaCl_2$), both in a volume ratio of 1:2.5 soil:solvent. The fourth subsample was prepared for the analyses using the sensor system in manual mode, with the addition of deionised water to obtain the same soil:water ratio of the samples sent to the laboratory. The pH values that were read by the sensor system in manual mode were compared to the average of the respective pH values determined in the three laboratories ($pH_{L1}$, $pH_{L2}$, and $pH_{L3}$) in water and in 0.01 N $CaCl_2$.

The pH data obtained by sensing in automatic mode were compared with the pH results in water and the pH results in $CaCl_2$ that were measured in the laboratory; they were designated $pH_{LW}$ and $pH_{LC}$, respectively.

The coordinates of the georeferenced soil samples were located using a geographic information system (GIS). Small circular zones with 12.0 m radius were demarcated around the coordinates to cover the closest pH points collected by the automatic sensor system. Within each of these areas, the average for the measurements was calculated ($pH_{as}$) and compared with the corresponding average obtained in the laboratory using the mean absolute error ($MAE_{auto}$), which was calculated according to equation 1.

$$MAE_{auto} = \frac{1}{n}\sum_{1}^{n}\left|pH_{as} - pH_{lab}\right| \qquad (1)$$

where $pH_{as}$ is the average pH value determined by automatic sensor system; $pH_{Lab}$ is the average between $pH_{L1}$, $pH_{L2}$, and $pH_{L3}$, which correspond to the pH values determined in water ($pH_{LW}$) and in 0.01 N $CaCl_2$ ($pH_{LC}$), which were separately obtained in laboratory and calculated.

Electrochemical sensors require a particular time period for the sensing element to reach equilibrium with the soil or measured soil solution, which varies according to the type of electrode (Viscarra Rossel et al., 2005). To assess the response time of the electrodes, five soil samples that were obtained by grid sampling were preselected and individually placed in direct contact with the two antimony electrodes to analyse the required time to achieve an equilibrium, which is referred to as the response time. The operation was timed, and the pH values were recorded while simulating the response times of 5 s, 10 s, 20 s, 30 s, and 60 s, each one with ten replicates. The ideal required time for electrodes to stabilise during the pH reading was determined using the root mean square error of pH values as a function of response time ($RMSE_t$), as determined by equation 2, followed by Student's t-test.

$$RMSE_t = \sqrt{\sum_{1}^{n}\left(pH_{resp} - pH_{lab}\right)^2 / n} \qquad (2)$$

where $pH_{resp}$ is the average of ten pH measurements, separately obtained for 5 s, 10 s, 20 s, 30 s, and 60 s; $pH_{Lab}$ is the pH value for both solvents, determined in the laboratory; and n is the number of soil samples used for analysing the response time (in this case, five samples).

The precision of the measurement refers to the reproducibility of the obtained values for ion activity in similar conditions. The calculation was performed based on the pH readings, which were separately recorded for each of the electrodes in the measurements, with ten replicates for each of the three points that were sampled at a response time of 20 s, which is the standard time set by the system manufacturer. The precision measurement was quantified by the root mean square error of precision ($RMSE_p$).

$$RMSE_p = \sqrt{\sum_{1}^{n}\left(pH_{ms} - \overline{pH}_{ms}\right)^2 / n} \qquad (3)$$

where pHms and pHms are the pH value obtained with sensor in manual mode and mean for all pH readings, respectively; and n is the number of readings.

The accuracy of a given equipment is its capacity to express values that are identical to the values that are established as real. For measuring accuracy, ten replicates were obtained from each sampling point, using the records of the sensor at a response time of 20 s. For the manual mode, the quantification of accuracy was performed by the $RMSE_a$ for the pH values determined by the sensor in real time and the respective $pH_{Lab}$ value, which is divided by the number of degrees of freedom (n) and expressed by equation 4.

For the automatic mode, accuracy was calculated by $MAE_{auto}$, as described on equation 1.

$$RMSE_a = \sqrt{\sum_1^n (pH_{ms} - pH_{lab})^2 / n} \quad (4)$$

Calibration lines were constructed based on manual and automatic operating modes for each one of the different areas, to which were designated specific calibration lines. Simple regression using the pH results determined by the sensor system and the laboratory techniques were performed. The points on each specific curve for a given parameter were employed to construct calibration lines for the set of areas, which were designated as general calibration lines.

To assess the effectiveness of the calibration lines, a validation phase, in which ten new soil sampling points (validation points) were randomly selected in each area, was conducted. The pH values obtained using the sensor system that corresponded to the values obtained in the laboratory were identified on the calibration curve. Mean absolute errors were calculated for pre- and post-calibration validation points and were designated $MAE_B$ and $MAE_{Cal}$, respectively.

$$MAE_B = \frac{1}{n}\sum_1^n \left| pH_{val} - pH_S \right| \quad (5)$$

$$MAE_{Cal} = \frac{1}{n}\sum_1^n \left| pH_{val} - pH_{Scal} \right| \quad (6)$$

where $pH_{val}$ is the pH value determined in the laboratory for the validation point; $pH_S$ is the pH value determined by the sensor in real time (raw data point); and $pH_{Scal}$ is the $pH_S$ value determined for the calibration curve for the allocated raw data.

The quantitative indicators of the calibration lines were their determination coefficients ($R^2$), followed by the F-test (Fisher-Snedecor) to determine the homogeneity of variances, using 5% as the level of significance.

Analyses were complementarily performed under control conditions to test the interference of soil water content during pH measuring in real time. The experiment, which followed a completely randomised design, was composed of fifteen soil samples that were manually collected at a depth of 0.1 m. The treatments corresponded to the mean moisture content of soil, which ranged from field capacity to the permanent wilting point. The tested moisture levels in volume/volume percentage, which were attained by adding water to the dry and ground samples, were equivalent to 10, 20, and 40%. After adding each portion of water, the samples were allowed to rest to reach equilibrium. They were subsequently subjected to a pH reading. As with all steps performed in this study, the results for pH as a function of moisture underwent an analysis of variance, and the means were compared by Tukey's t-test, using R software (The R Foundation, 2014).

## Results and Discussion

### Real-time soil mapping under automatic mode

The measurements obtained using the sensor system in automatic mode consisted of approximately 500 points, which were sampled in areas 1 and 2, and 700 points, which were sampled in area 3. They correspond to a sampling density of 45 data per hectare. Loamy soils had more limitations with regards to the sampler's operation, which has problems of soil stuck to it, and sporadic obstructions, especially in high moisture conditions. It is expected that real-time sampling by the system does not follow a moisture standard, changing along the landscape. The shape of the sampling device should be taken into consideration, such as a larger diameter, to facilitate the movement of the soil inside the sampler.

The mean values obtained by the equipment ($pH_{as}$) and the corresponding maximum and minimum pH values tended to be overestimated compared with the pH values determined in water and calcium chloride ($pH_{LC}$), with the $pH_{LC}$ values lower for a given area. These results were already expected, given the lower ionic activity in these conditions (Little, 1992).

As shown in Table 2, the mean difference between the $pH_{as}$ and $pH_{LW}$ values was 0.92 pH unit for area 1, where the difference between $pH_{as}$ and $pH_{LC}$ reached 1.60 unit. In area 2, the difference between the readings was lower, which corresponds to 0.62 and 1.21 for $pH_{LW}$ and $pH_{LC,}$ respectively, for readings using the sensor system. For this same area, the difference between the two methods was almost two-fold greater compared with area 1. Table 3 confirms that the mean difference between the $pH_{as}$ and $pH_{Lab}$ values was greater in loamy soils; a similar condition was observed for the mean absolute errors. For area 3, which is characterised by soil with a medium-sandy texture, the $MAE_{auto}$ for the samples determined in water ($pH_{LA}$) and calcium chloride ($pH_{LC}$) varied between 0.34 and 1.15 pH unit.

### Ion-selective electrode performance – response time, precision, and accuracy

The RMSE values for each reading time, for samples from the three experimental areas, are presented on Table 4. For the evaluated reading-stabilisation times, the ten initial seconds corresponded to the period with the greatest instability of values and exhibited a mean variation of 0.5 pH unit for area 1. The mean reading difference between electrodes corresponded to 0.24 pH unit, which was equivalent to 4% of variation and did not significantly differ between reading-stabilisation times. Results were less stable on the soil with higher clay content (area 2), characterized as higher sum of bases. Contrarily, the results in the sandy soil (area 3) did not show substantial instability in readings of the sensor system over time, but showed better performance, with smaller differences in the readings between the pair of electrodes. It is suggested that granulometric and mineralogical fraction of the soil are related to the results, as the evaluated Oxisol, with medium texture, may offer less mineralogical variability in the clay fraction, which submitted the samples to the lower interference of functional groups present on the surface of suspended minerals in the soil solution in the pH determination process, as indicated by Inda Junior & Kämpf (2005).

Note that the samples in this area had the highest pH values, which may have contributed to less overestimation by the sensor system. The period from 10 to 30 s showed statistically equivalent readings. After this period, measurement by electrodes yielded a reduction in the recorded pH values, which were statistically equivalent to the values obtained in the initial 10 s of reading.

With regard to precision, Table 5 shows that the soil samples from area 1 exhibited deviations between 0.1 and 0.8 pH unit. This difference was more pronounced for area 2, with greater differences between readings for a given point sampled. The electrodes performed better in area 3, due to possible soil fraction characteristics, already discussed. Precision did not differ within each pair of electrodes and each experimental area. The calculated values are not within the precision range that is considered ideal by standardisation entities for chemical laboratory analysis. Technical standard NBR 7353 establishes a variation of ±0.02 pH unit as a reproducible value for measurements with a 95% confidence interval (Associação Brasileira de Normas Técnicas, 2014). However, the acceptable error depends on the particular requirement of the experiment and the purpose of the result. For the majority of analytical laboratories, an error of ±0.1 pH unit is acceptable.

The pH results obtained in real-time show higher variability regarding moisture in the collected samples and lower equilibrium of the soil-solution system compared with samples that were analysed in the laboratory. Considering those conditions and the precision obtained for the three areas, the system has potential and should be improved to achieve better results.

With regard to the accuracy of the obtained values for the three experimental areas, the electrodes were sensitive to the $H^+$ ions of samples. As shown in Figure 2, the linear curves always remained in the same direction of increase or decrease of the pH values obtained in the laboratory, particularly in the case of

**Table 2.** Descriptive analysis of the data obtained in automatic operating mode for pH measurement in the three experimental areas.

| Descriptive analysis | $pHa_S$ | $pH_{LW}$ | $pH_{LC}$ | $pHa_S$ | $pH_{LW}$ | $pH_{LC}$ | $pHa_S$ | $pH_{LW}$ | $pH_{LC}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mean | 5.79 | 4.87 | 4.19 | 6.07 | 5.45 | 4.86 | 6.15 | 5.81 | 5.00 |
| Minimum | 5.28 | 4.35 | 3.68 | 5.48 | 4.85 | 4.30 | 5.60 | 5.20 | 4.50 |
| Maximum | 7.16 | 6.57 | 5.81 | 6.60 | 6.00 | 5.40 | 7.00 | 6.40 | 5.60 |
| Median | 5.74 | 4.75 | 4.07 | 6.02 | 5.52 | 4.90 | 6.20 | 5.80 | 4.95 |
| Standard deviation | 0.38 | 0.43 | 0.41 | 0.33 | 0.35 | 0.32 | 0.30 | 0.32 | 0.33 |
| Coefficient of variation (%) | 6.51 | 8.90 | 9.67 | 5.41 | 6.44 | 6.66 | 4.85 | 5.45 | 6.54 |
| Asymmetry | 1.38 | 1.99 | 2.05 | -0.33 | -0.36 | -0.21 | 0.82 | -0.12 | 0.15 |
| Kurtosis | 0.07 | 0.11 | 0.13 | 0.00 | -0.04 | -0.03 | 0.18 | -0.01 | -0.03 |

samples with higher pH values. An accuracy of 0.44 was obtained for area 1, regarding data measured in water in the laboratory. Accuracies of 0.55 and 0.74 were obtained for area 2 (loamy) and area 3 (medium-sandy), respectively. This error was greater than the error obtained for the pH of calcium chloride, which corresponds to 1.1 for the first two areas and 1.48 for area 3. Higher contents of clay may have contributed

**Table 3.** Mean absolute errors (MAE) for the reference pH values and pH values determined by the sensor system in automatic mode(1).

| Reference pH | Experimental area | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| $pH_{LA}$ | 0.91a* | 0.70a | 0.34a |
| $pH_{LC}$ | 1.60b | 1.21b | 1.15b |

(1)Means followed by equal letter in the column do not differ by Tukey's test at 5% probability.

**Table 4.** Comparisons of root mean square error of pH values as a function of response time ($RMSE_t$) for the three experimental areas(1).

| Sample | Electrode | Response times (s) | | | | |
|---|---|---|---|---|---|---|
| | | 5 | 10 | 20 | 30 | 60 |
| | | | | Area 1 | | |
| 01 | 1 | 0.657a | 0.911b | 0.996b | 0.996b | 0.916b |
| | 2 | 0.358c | 0.618a | 0.663a | 0.663a | 0.374c |
| 02 | 1 | 0.923a | 1.081a | 1.122a | 1.122a | 1.006a |
| | 2 | 0.569b | 0.762b | 0.762b | 0.762b | 0.684b |
| 03 | 1 | 0.668a | 0.764a | 0.781a | 0.762a | 0.700a |
| | 2 | 0.512a | 0.566a | 0.581a | 0.581a | 0.500a |
| 04 | 1 | 0.621a | 0.721a | 0.742a | 0.703a | 0.621a |
| | 2 | 0.522a | 0.621a | 0.600a | 0.600a | 0.500a |
| 05 | 1 | 0.546a | 0.662a | 0.681a | 0.642a | 0.585a |
| | 2 | 0.447a | 0.542a | 0.542a | 0.562a | 0.463a |
| | | | | Area 2 | | |
| 01 | 1 | 0.303a | 0.261a | 0.344a | 0.341a | 0.374a |
| | 2 | 0.447b | 0.525b | 0.504b | 0.422b | 0.397a |
| 02 | 1 | 0.394ab | 0.453ab | 0.572a | 0.643a | 0.624a |
| | 2 | 0.278b | 0.378ab | 0.341ab | 0.311ab | 0.200b |
| 03 | 1 | 0.504a | 0.681a | 0.841ab | 0.900b | 0.923b |
| | 2 | 0.841ab | 0.881ab | 0.800ab | 0.700ab | 0.482a |
| 04 | 1 | 0.120a | 0.253a | 0.330a | 0.373a | 0.330a |
| | 2 | 0.293a | 0.216a | 0.293a | 0.392a | 0.573b |
| 05 | 1 | 0.655ab | 0.811a | 0.992a | 1.031a | 1.051a |
| | 2 | 0.153b | 0.186b | 0.153b | 0.085b | 0.192b |
| | | | | Area 3 | | |
| 01 | 1 | 0.422a | 0.673ab | 0.852b | 0.877b | 0.861b |
| | 2 | 0.357a | 0.529ab | 0.670ab | 0.640ab | 0.618ab |
| 02 | 1 | 0.291a | 0.516b | 0.657b | 0.673b | 0.694b |
| | 2 | 0.225a | 0.392a | 0.470b | 0.512b | 0.512b |
| 03 | 1 | 0.733ab | 0.951a | 1.069a | 1.105a | 1.105a |
| | 2 | 0.690b | 0.843a | 0.923a | 0.962a | 0.862a |
| 04 | 1 | 0.664a | 0.783a | 0.826a | 0.803a | 0.783a |
| | 2 | 0.628a | 0.744a | 0.801a | 0.801a | 0.764a |
| 05 | 1 | 0.504a | 0.365ab | 0.397ab | 0.436a | 0.482a |
| | 2 | 0.613a | 0.259b | 0.202b | 0.202b | 0.147b |

(1)Means followed by equal letter in the same row do not differ by Tukey's test at 5% probability.

to the instability, greater ionic activity during the real-time measurements, and larger errors. Student's t-test showed a statistically significant difference between the two operating modes of the equipment for the two clayey areas.

Results from area 3 did not reveal a difference between the two operating modes. The accuracy of the sensor system in the automatic operating mode was greater in the medium-sandy soil when the results between the experimental areas and their respective soils were compared (Table 6). In contrast to expectations, high accuracy was not observed in the results obtained in the manual operating mode in area 3. As the samples were standardised and reached equilibrium prior to measuring the pH in manual mode, this process may have reduced the variation in the chemical stability between samples.

Compared with the studies of Schirrmann et al. (2011), a possible explanation for the inferior performance of the sensor in the experimental conditions is the different soil characteristics and the peculiar behaviour of soils that are naturally acidic, particularly due to the long time period during which they were exposed to the action of rain and sun, which conferred a lower cation exchange capacity and low buffer power. In this case, high correlations were obtained between the data obtained in the laboratory and the data obtained with the sensor system. The soils of the experimental areas in a typically temperate climate were characterised by the predominance of a silt fraction free of variable charges. Also in temperate soils, Sethuramasamyraja et al. (2007), when quantifying the performance of the electrodes of the same pH sensor system, obtained relatively constant precision between the soils and favorable accuracy for the pH electrodes. The RMSE for commercial laboratory data was 0.21 pH. The results showed an excellent correlation with the reference electrodes ($R^2$>0.9) for pH electrodes, showing that the ISE has potential for use in precision agriculture.

**Table 5.** Error indicators: root mean square error of precision ($RMSE_p$) and relative error, which correspond to the precision of the two electrodes (E1 and E2) that compose the sensor system in manual operating mode in the three experimental areas (A1, A2, and A3)(1).

| Error indicators | A1 | | A2 | | A3 | |
|---|---|---|---|---|---|---|
| | E1 | E2 | E1 | E2 | E1 | E2 |
| $RMSE_p$ | 0.121a | 0.173a | 0.091a | 0.106a | 0.123a | 0.147a |
| Relative error (%) | 2.3 | 3.4 | 1.5 | 1.8 | 1.9 | 2.4 |

(1)Means followed by equal letter in a row do not differ by Tukey's test at 5% probability.

Despite the limited knowledge about the factors determining the stability of organomineral complexes in soils, this has been related to the type and intensity of interactions between minerals and organic matter constituents (Cornejo & Hermosin, 1996) as well as the organic matter content (Stevenson, 1994), which positively affects the stability of the complexes in clayey soils (Bayer et al., 2002). This fact is important to be considered for the lower performance results found in the pH sensing for the three Oxisols, which, oxidized, presented very low organic matter content, especially when compared to temperate soils, under favorable conditions for production of organic matter.

## Calibration

Evaluating the sensing on automatic mode, when a simple linear regression was applied to the pH values obtained in the three areas against the corresponding laboratory data, the data were not strictly linear (Figure 2). The correlation lines did not yield a good fit, as evidenced by the low determination coefficients.

**Table 6.** Comparisons between the parameters related to accuracy, calculated for the sensor system in manual and automatic operating modes in the three experimental areas (A1, A2, and A3)(1).

| Operating mode | Parameter | A1 | | A2 | | A3 | |
|---|---|---|---|---|---|---|---|
| | | $pH_{LW}$ | $pH_{LC}$ | $pH_{LW}$ | $pH_{LC}$ | $pH_{LW}$ | $pH_{LC}$ |
| Manual | RMSE | 0.44a* | 1.10b | 0.55a | 1.11b | 0.74ab | 1.48c |
| Automatic | $MAE_{auto}$ | 0.91b | 1.60c | 0.68ab | 1.18b | 0.48a | 1.27bc |

(1)Means followed by equal letter in a column do not differ by Tukey's test at 5% probability.

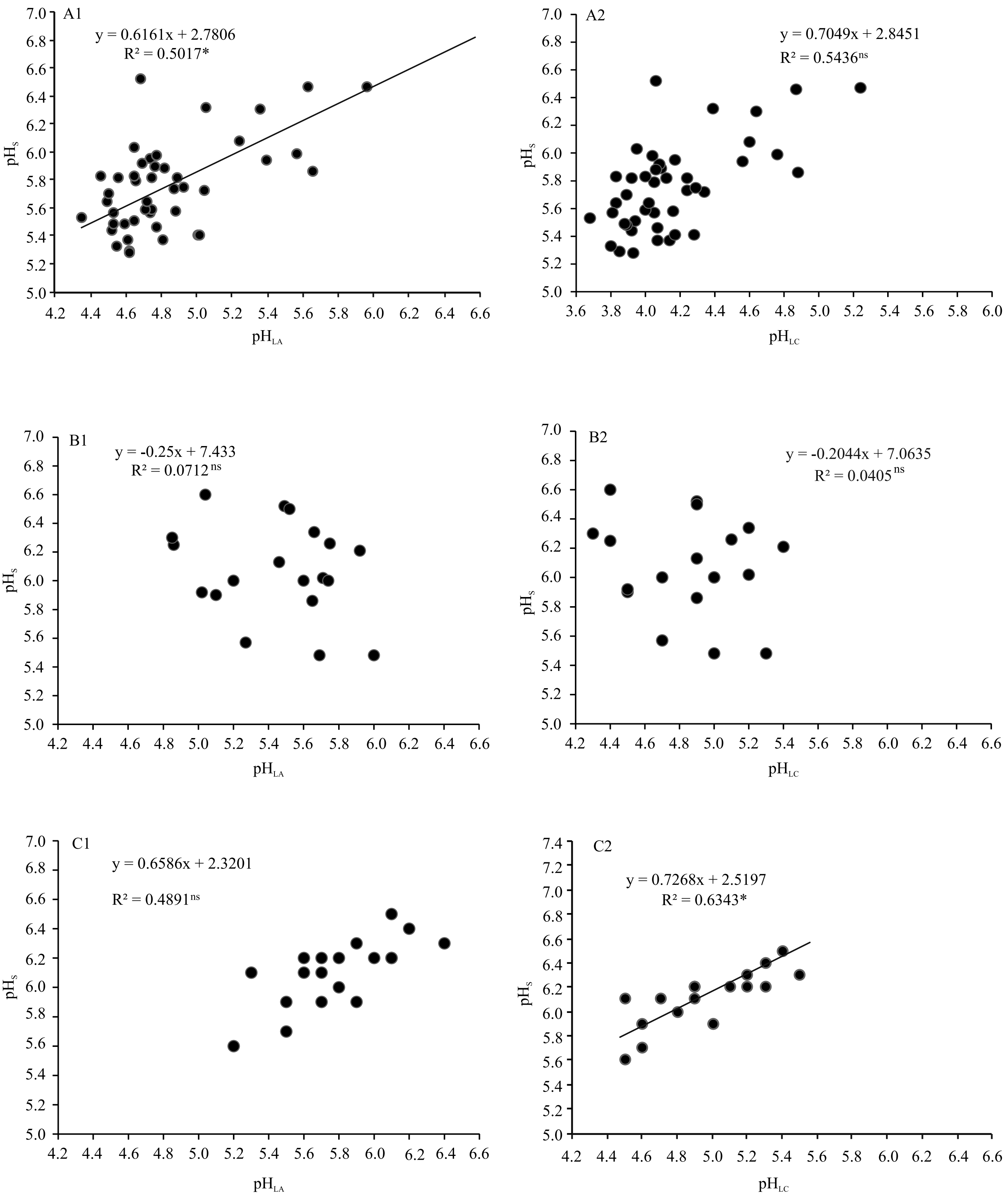


**Figure 2.** Regressions of pH values that were obtained in the laboratory (1) and real time (2) with the automatic sensor system: (A) area 1, (B) area 2, and (C) area 3. $pH_S$, pH value determined by real time sensor; $pH_{LW}$, pH values determined in water; and $pH_{LC}$, pH values determined in 0.01 N $CaCl_2$. $^{ns}$Nonsignificant. *Significant at 5% probability.

The pH data obtained in area 2, which was characterised as eutrophic Oxisol, did not yield significant regressions. In area 3, the determination coefficients were high, with the relationship between $pH_s$ and $pH_{LC}$ characterised by an $R^2$ of 0.63. At the level of significance of 0.05, the null hypothesis was only rejected for two of six regressions: the regressions that involve $pH_{LA}$ and $pH_{LC}$ in area 1 and area 3, respectively.

Different pH values were obtained for a single reference pH value for all lines. The determination coefficients indicate an inferior performance of electrodes in the soils of the experimental areas. The regression lines generated for the three areas, which corresponded to the data obtained using the automatic operating mode of the sensor system, did not provide support for accepting the initial hypothesis. The areas that contain soils with neutral or higher pH values also contribute to the higher stability of readings and the greater effectiveness of the calibration lines, as shown by Adamchuk et al. (2007). The variability of soil temperature and moisture in the field may contribute to explain this result in tropical soils. These two variables are not controlled during the sampling process in the field, unlike the process using laboratory techniques.

Samples were prepared in distilled water in standard laboratory soil-water ratios to determine pH using the sensor system in manual mode. Regression curves that were always significant at a 95% confidence interval and above 0.65 were obtained for all three areas (Figure 3). Regarding accuracy, the regression lines in area 3 yielded better results.

Determination coefficients converged with the $RMSE_a$ values, which indicated a better performance of the sensor in controlled conditions. This result was expected, given the greater homogenisation and standardisation of the samples that were analysed for pH. For both available operating modes, the obtained errors surpassed the value for precision and accuracy that is required by regulatory entities of soil analysis laboratory procedures. Loamy soils showed the largest reading errors due to the greater instability of these soils and the greater presence of interfering colloidal substances at the electrode-solution interface.

The small errors observed in the manual operating mode highlight the alternative of developing tools to directly standardise samples in the field, which is similar to the standardisation performed in the laboratory. The pH data that was determined in real time closely resembled the laboratory results for soil pH in water; this finding simplifies the standardisation process, as only the addition of water to samples in the field is required.

Figures 4 and 5 indicate that calibration lines that encompass the points of the three areas improved the final pH data that were obtained for both operating modes. The best correlation indices were achieved when calibrating the data obtained in the manual operating mode.

The specific and general calibrations enabled reduced deviations in the errors and reduction of extreme values for pH, which reduced the error distribution; this finding supports the results obtained by Schirrmann et al. (2011). However, the validation calculations presented in Table 7 show that the calibration lines did not effectively assure the accuracy obtained by conventional pH measuring equipment and methods. When comparing the two operating modes, a lower effectiveness of calibrations was observed for the samples collected in the manual operating mode.

The measurement of pH in real time for different soil moisture conditions confirmed the hypothesis that readings vary with the soil water content. For the three tested moisture levels, differences were observed between the respective means and variances at a 95% confidence level (Figure 6). The pH values proportionally increased with increased moisture content and varied by as much as 0.9 pH unit with a change in moisture range.

The results differed from those obtained by Adamchuk et al. (1999), who examined the effect of soil moisture on pH measurements, for which differences between pH readings for samples with physically feasible soil water contents (15 to 30%) were not observed. Although the three soils in this study belong to the wide-ranging order of Oxisols, they represent a small fraction of the soil classes that exist in the tropics. According to the level of detail adopted for soil classification, this fraction can be composed of hundreds of distinct soils. This diversity highlights the need for additional studies of the distinct characteristics of different soils.

Considering the concept of soil pH as a constituent of acidity that results from the release of hydrogen atoms into the soil by dissociation of its liquid phase, the importance of moisture as a factor in pH

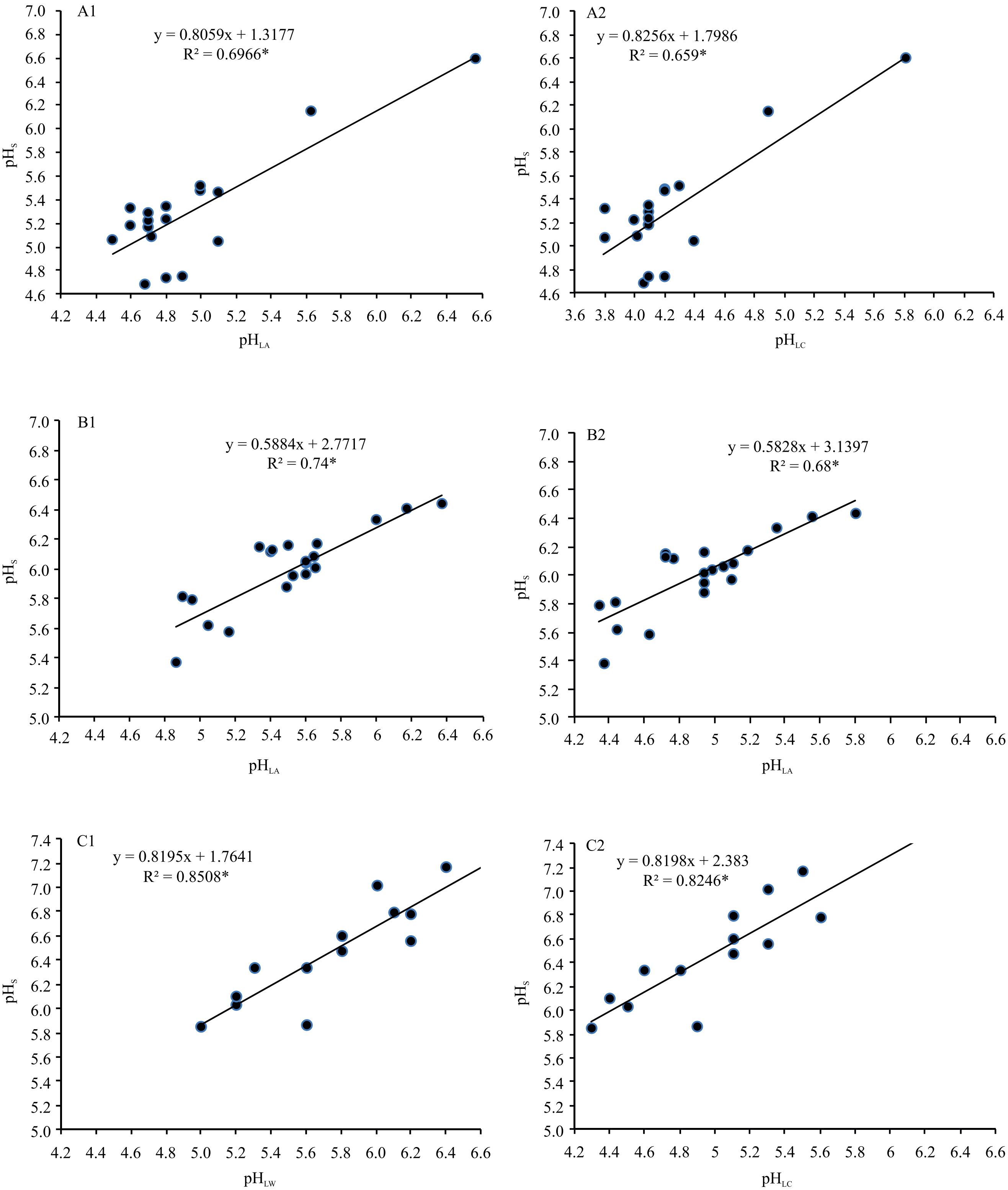


**Figure 3.** Regression for pH values determined by the sensor system in manual mode (1) and in a laboratory (2): (A) area 1, (B) area 2, and (C) area 3. pH$_s$, pH value determined by real time sensor; pH$_{LW}$, pH values determined in water; and pH$_{LC}$, pH values determined in 0.01 N CaCl$_2$. $^{ns}$Nonsignificant. *Significant at 5% probability.

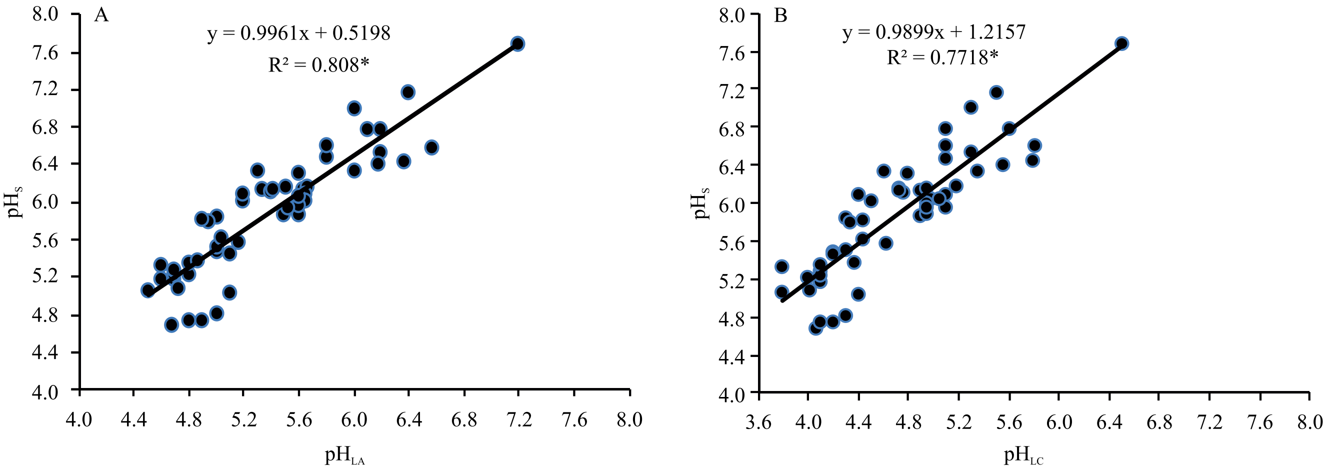


**Figure 4.** Regressions for general calibration of pH values obtained in (A) water and (B) calcium chloride in a laboratory, which were constructed for the sensor system in manual operating mode. $pH_s$, pH value determined by real time sensor; $pH_{LW}$, pH values determined in water; and $pH_{LC}$, pH values determined in 0.01 N $CaCl_2$. $^{ns}$Nonsignificant. *Significant at 5% probability.

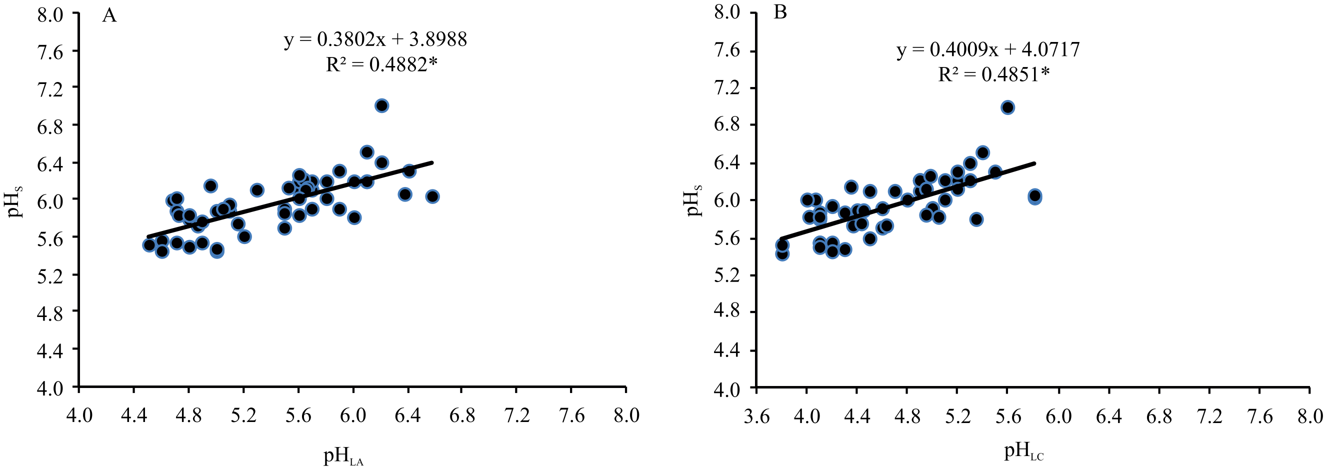


**Figure 5.** Regressions for the general calibration of pH values obtained in (A) water and (B) calcium chloride in the laboratory, which were constructed for the sensor system in automatic operating mode. $pH_s$, pH value determined by real time sensor; $pH_{LW}$, pH values determined in water; and $pH_{LC}$, pH values determined in 0.01 N $CaCl_2$. $^{ns}$Nonsignificant. *Significant at 5% probability.

**Table 7.** Mean absolute error (MAE) calculated in the validation phase for the two sensor system operating modes⁽¹⁾.

| Experimental area | Analysis | Operating mode | Pre-calibration | Post-specific calibration | Post-general calibration |
|---|---|---|---|---|---|
| 1 | $pH_{LW}$ | Auto | 0.72a | 0.89a | 0.85a |
| | | Manual | 0.51b | 0.39b | 0.11a |
| | $pH_{LC}$ | Auto | 1.45a | 1.61a | 1.56a |
| | | Manual | 1.20b | 0.52a | 0.65a |
| 2 | $pH_{LW}$ | Auto | 0.31a | 0.43a | 0.25a |
| | | Manual | 0.61a | 0.45a | 0.18a |
| | $pH_{LC}$ | Auto | 0.68a | 0.59a | 0.85a |
| | | Manual | 1.08a | 0.69b | 0.47b |
| 3 | $pH_{LW}$ | Auto | 0.67a | 0.38a | 0.40a |
| | | Manual | 0.81a | 0.74a | 0.24b |
| | $pH_{LC}$ | Auto | 1.34a | 1.18a | 1.13a |
| | | Manual | 1.49a | 0.88ab | 0.29b |

(1)Means followed by equal letter in a row do not differ by Tukey's test at 5% probability.

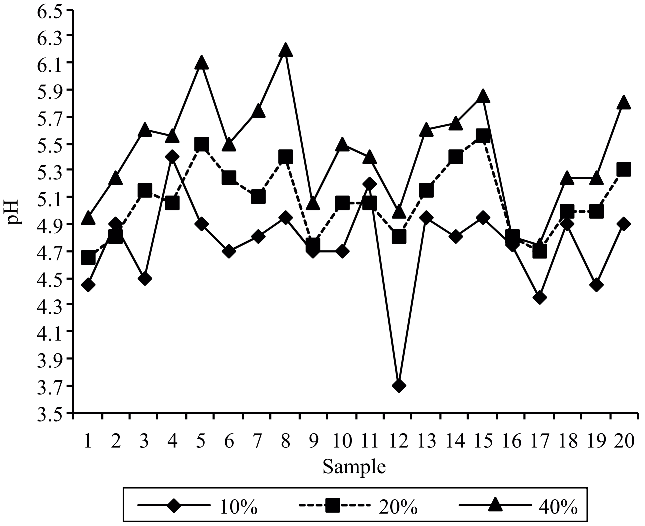


**Figure 6.** Variation in the pH measured in real time for the same samples as a function of different moisture levels.

readings is confirmed for the analysed technique. This finding suggests that soil moisture content should be considered an issue when measuring pH in real time.

## Conclusions

1. The measurement of pH in real time by antimony ISE in the study areas are not equivalent to corresponding laboratory measurements, regardless of the chemical characteristics and textures of the soils.
2. The minimum time of 20 s, as indicated by the manufacturer for electrode contact with soil, corresponded to the results; however, accuracy and precision fall outside of the error interval that is allowed by laboratory soil analysis standardisation entities.
3. More promising results are observed for pH measurements in real time in manual operating mode, which indicates the need for homogenisation and standardised sample moisture at the time of measuring it.
4. The sensor system yield sampling density of 45 data per hectare represents a great contribution to the intensification of data for better spatial evaluation of soil information.

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## References

ADAMCHUK, V.I.; LUND, E.D.; REED, T.M.; FERGUSON, R.B. Evaluation of on-the-go technology for soil pH mapping. **Precision Agriculture**, v.8, p.139-149, 2007. DOI: 10.1007/s11119-007-9034-0.

ADAMCHUK, V.I.; MORGAN, M.T.; ESS, D.R. An automated sampling system for measuring soil pH. **Transactions of the ASAE**, v.42, p.885-891, 1999. DOI: 10.13031/2013.13268.

ADAMCHUK, V.I.; MORGAN, M.T.; LOWENBERG-DEBOER, J.M. A model for agro-economic analysis of soil pH mapping. **Precision Agriculture**, v.5, p.111-129, 2004. DOI: 10.1023/B:PRAG.0000022357.28154.eb.

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. **NBR 7353**: soluções aquosas: determinação do pH com eletrodos de vidro. Rio de Janeiro, 2014. 8p.

BAYER, C.; DICK, D.P.; RIBEIRO, G.M.; SCHEUERMANN, K.K. Stocks and humification degree of organic matter fractions as affected by no-tillage on a subtropical soil. **Plant and Soil**, v.238, p.133-140, 2002. DOI: 10.1023/A:1014284329618.

BROUDER, S.M.; HOFMANN, B.S.; MORRIS, D.K. Mapping soil pH: accuracy of common soil sampling strategies and estimation techniques. **Soil Science Society of American Journal**, v.69, p.427-442, 2005. DOI: 10.2136/sssaj2005.0427.

CAIRES, E.F.; GARBUIO, F.J.; CHURKA, S.; BARTH, G.; CORRÊA, J.C.L. Effects of soil acidity amelioration by surface liming on no-till corn, soybean, and wheat root growth and yield. **European Journal of Agronomy**, v.28, p.57-64, 2008. DOI: 10.1016/j.eja.2007.05.002.

COLLINS, K.; CHRISTY, C.; LUND, E.; DRUMMOND, E. **Developing an automated soil pH mapping system**. St. Joseph: ASAE, 2003. (Paper n. MC03-205).

CORNEJO, J.; HERMOSIN, M.C. Interaction of humic substances in soil clays. In: PICCOLO, A. (Ed.). **Humic substances in terrestrial ecosystems**. Amsterdam: Elsevier, 1996. p.595-624. DOI: 10.1016/B978-044481516-3/50016-5.

FONTES, M.P.F.; CAMARGO, O.A. de; SPOSITO, G. Eletroquímica das partículas coloidais e sua relação com a mineralogia de solos altamente intemperizados. **Scientia Agricola**, v.58, p.627-646, 2001. DOI: 10.1590/S0103-90162001000300029.

GEBBERS, R.; ADAMCHUK, V.I. Precision agriculture and food security. **Science**, v.327, p.828-831, 2010. DOI: 10.1126/science.1183899.

GEBBERS, R.; HERBST, R.; WENKEL, K.-O. Sensitivity analysis of soil nutrient mapping. In: JOINT INTERNATIONAL AGRICULTURAL CONFERENCE, 7., 2009, Wageningen. **Proceedings**. Wageningen: Wageningen Academic Publishers, 2009. p.513-519.

INDA JUNIOR, A.V.; KÄMPF, N. Variabilidade de goethita e hematita via dissolução redutiva em solos de região tropical e subtropical. **Revista Brasileira de Ciência do Solo**, v.29, p.851-866, 2005. DOI: 10.1590/S0100-06832005000600003.

JOO, S.; BROWN, R.B. Chemical sensors with integrated electronics. **Chemical Reviews**, v.108, p.638-651, 2008. DOI: 10.1021/cr068113+.

KHOSLA, R.; WESTFALL, D.G.; REICH, R.M.; MAHAL, J.S.; GANGLOFF, W. Spatial variation and site-specific management zones. In: OLIVER, M.A. (Ed.). **Geostatistical applications for precision agriculture**. Dordrecht: Springer, 2010. p.195-219. DOI: 10.1007/978-90-481-9133-8_8.

LITTLE, I.P. The relationship between soil pH measurements in calcium-chloride and water suspensions. **Australian Journal of Soil Research**, v.30, p.587-592, 1992. DOI: 10.1071/SR9920587.

SCHIRRMANN, M.; GEBBERS, R.; KRAMER, E.; SEIDEL, J. Soil pH mapping with an on-the-go sensor. **Sensors**, v.11, p.573-598, 2011. DOI: 10.3390/s110100573.

SETHURAMASAMYRAJA, B.; ADAMCHUK, V.I.; MARX, D.B.; DOBERMANN, A.; MEYER, G.E.; JONES, D.D. Analysis of an ion-selective electrode based methodology for integrated on-the-go mapping of soil pH, potassium, and nitrate contents. **Transactions of the ASABE**, v.50, p. 1927-1935, 2007.

SORATTO, R.P.; CRUSCIOL, C.A.C. Nutrição e produtividade de grãos da aveia-preta em função da aplicação de calcário e gesso em superfície na implantação do sistema plantio direto. **Revista Brasileira de Ciência do Solo**, v.32, p.715-725, 2008. DOI: 10.1590/S0100-06832008000200026.

STEVENSON, F.J. **Humus chemistry**: genesis, composition, reactions. 2nd ed. New York: J. Wiley, 1994. 512p.

THE R FOUNDATION. **R**: the R project statistical computing. Vienna: R Foundation for Statistical Computing, 2014.

VISCARRA ROSSEL, R.A.; GILBERTSON, M.; THYLÉN, L.; HANSEN, O.; MCVEY, S.; MCBRATNEY, A.B. Field measurements of soil pH and lime requirement using an on-the-go soil pH and lime requirement measurement system. In: EUROPEAN CONFERENCE ON PRECISION AGRICULTURE, 5., 2005, Uppsala. **Proceedings**. Wageningen: Academic Publishers, 2005. p.511-520.

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