

Soil Calcium and pH Monitoring Sensor System

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An agrarian sensorial system based on temperature, moisture, and all solid-state ion-selective potentiometric sensors was developed with the objective of monitoring the behavior of H⁺ and Ca²⁺ ions in soil and in real conditions, contributing with a new tool that tries to complement the current precision agriculture technology. The evaluation of the sensorial system to pH monitoring presented a good correlation between the results obtained by the system and the standard methodology, allowing us to notice the soil buffer capacity at different soil depths. With regard to calcium, the sensor system also presented an agreement between its results and those obtained by flame atomic absorption spectrometry, using a calibration model based on multiple linear regressions that allows the correct determination of Ca²⁺ concentrations in soil depths where the relative moisture is different. In this way, using well-known potentiometric sensors in a complex, discontinued, and heterogeneous matrix, such as soil, the sensorial system proved to be a useful task for agrochemical field applications.

KEYWORDS: pH; calcium; in situ soil analysis; potentiometric sensor; precision agriculture

INTRODUCTION

At the present time, different technologies have been applied in agriculture with the aim of increasing the production and diminishing the environmental impact in edaphic waters produced by excessive fertilizer contribution. The management systems of agricultural production—precision agriculture—have become one of the main tools in the construction of productivity maps that provide useful and effective information for the handling of extensive zones of cultures. Among the used tools to complement this technology are aerial photographs, satellite images, and collection of soil samples. The developed technology allows a much more effective dosing of fertilizers, considerably increasing the productivity of the harvest. However, it also has certain limitations and errors. The productivity maps are constituted from a delayed sample from the point of view of intervention in the handling of the culture. The productivity also presents temporal variability, and the available equipment has certain limitations in their exactitude; necessary adjustments are made after generation of data in the field (1–6).

Current tendencies for precision agriculture point to obtaining continuous in situ information about soil physical and chemical parameters, such as macro- and micronutrients, because of

modulation of the amounts of fertilizers to be added. The most promising instrumentation for soil analysis that has been developed belongs to the sensor field. In recent years, instrumentation based on direct contact or remote sensing performed in close proximity to the crop has been introduced. The advantages of sensors are their robustness, reduced size, versatility, and low mass production costs. They are simple devices, as compared with other analytical techniques such as chromatography or spectroscopy, and moreover, they offer the possibility of designing in situ analysis systems (7).

The objective of the present article is to propose an analytical sensor system able to obtain in situ and real-time measurements of the activity of the H⁺ and Ca²⁺ ions in soils. Soil pH is a factor that affects in a decisive way the assimilation process of different essential nutrients for the development of the cultures. Acid soils reduce the activity of the soil organic matter decomposing microorganisms, decreasing the liberation of N, P, and S, and also causing toxicity problems due to Al³⁺ ions (8). Calcium compounds are used to correct the soil pH. In this application, a great amount of calcium carbonate is usually applied as lime. Moreover, this ion is necessary in structural functions, reduces the soil compaction, activates different enzymatic systems that regulate the vegetal growth, and contributes to the increase of the harvest resistance to plagues and ailments (8).

The developed instrumentation is based on the connection of three all solid-state electrochemical sensors, three temperature sensors, and three moisture sensors at different heights with the

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required electronic instrumentation that allows the data acquisition and data transmission via radio. The potential profiles provided by the sensor system were compared to the results obtained by standard soil analysis methodologies. The pH was determined via potentiometry using a calcium chloride solution as the extractor and a combined glass electrode (9). Calcium analysis was performed after soil extraction with an ion-exchange resin (10) and determination was performed using flame atomic absorption spectrometry (FAAS) (11).

The generated information permits the monitoring of these parameters directly in soil, thus providing an immediate knowledge and possibility of making decisions for both ions in real time. This novel tool also tries to overcome certain existing limitations in current precision agriculture, since a few systems determining the necessities or deficiency of the soil nutrients in real or almost real time are depicted (12–14).

EXPERIMENTAL PROCEDURES

All Solid State pH and Calcium Sensors. Sensors were constructed as previously described in the literature (14). The pH membrane composition was (w/w) as follows: 32.8% PVC, 65.6% plasticizer [bis-(2-ethyl)sebacate], 1.0% hydrogen ionophore (tridodecylamine), and 0.6% of an ionic additive [potassium tetrakis(4-chlorophenyl)borate]. The calcium polymeric membrane composition was (w/w) as follows: 29.8% PVC, 63.2% plasticizer (di-*n*-octylphenylphosphonate), and 7.0% calcium ionophore {calcium bis[4-(1,1,3,3-tetramethylbutyl)phenyl phosphate]}, all acquired from Fluka (Switzerland).

Sensor System. The study of both chemical parameters was carried out separately using the same sensor system. The sensors set was made up of an electrochemical sensor (ion-selective electrode, ISE), a moisture sensor, and a temperature sensor. This was divided in two parts, an inferior one constituted by a PVC tube ($l = 120$ cm, $\varnothing_{\text{ext}} = 9$ cm) comprising a sensors set in a way that when the probe is inserted in the soil the sensors are located at 5, 20, and 50 cm of depth from the soil surface. The other part of the probe was composed of an airtight box, which holds necessary instrumentation for signal amplification and data transmission. The electrochemical sensor was located inside a copper plate that acted like a reference electrode (13, 14); depending on the sensor membrane used, one obtained the pH or calcium determination. Above the ISE, an orifice that connected by the inner part of the probe to a polyethylene tube served to inject pH or calcium standard solutions with the purpose of varying soil conditions when the probe was installed in the field, allowing the calibration process. The temperature sensor was an off-the-shelf sensor (LM35CZ, National Semiconductors, United States) that allowed measurement of the temperature from -55 up to $+150$ °C, with an accuracy of 0.5 °C. The moisture sensor was based on two copper antennas (10 cm length, 1 mm diameter) located in parallel and connected to the outer part of the PVC tube. Inside the PVC tube was installed the electrical circuitry in charge to amplify and lead the potentiometric and temperature sensor signals to the superior part of the probe, which has a voltage amplifier. A data acquisition system (15) was used to collect temperature and potential signals, convert them into digital data, and transmit them in real time via radio to a remote computer, where the data automatically filled an electronic worksheet. In the superior part also, there were BNC type connections coupled to a time-domain reflectometer (TDR) field equipment Tektronix 150X (Utah), which allowed the collect of moisture data (16).

Standard Soil Methodology for pH and Calcium Determination.

With the aim of comparing and later validating the results given by the electrochemical sensorial system, two standard soil analysis methodologies were used to determine pH and calcium. The standard method more used to determine soil pH was based on the preparation of a mixture of 10 g of ground and air-dried soil sample and a 0.05 mol L⁻¹ calcium chloride solution. It was shaken for 5 min and left to rest for a period of time neither inferior to 30 min nor superior to 3 h. After this period, the mixture was shaken once more and the pH of the suspension was measured with a combined glass electrode (17). Calcium

determination was carried out through an extraction with a mixed ion-exchange resin and analysis by FAAS (10, 11).

In-Soil Evaluation. In the first experimental stage, an external calibration of the sensor system was accomplished with the aim of observing the probe behavior as well as obtaining a correct process of polymeric membrane preparation and conditioning. Cotton soaked in different standard solutions of increasing concentration was used. Hydrogenphthalate buffer solutions and monobasic potassium phosphate with sodium hydrogencarbonate buffer solutions, all in concentrations of 1×10^{-2} mol L⁻¹, were used in the pH studies. The buffers covered a pH range between 3 and 10. With regard to calcium membrane, concentrations from 10^{-5} up to 10^{-1} mol L⁻¹ calcium chloride solutions were employed. The soaked cottons were placed over each set of sensors (different depths) in a way to cover all sensors of the set.

In a second experimental phase, an attempt to simulate the soil conditions was done. A setup was constructed with a PVC tube ($\varnothing_{\text{id}} = 12$ cm) containing three lateral openings, corresponding to the sensor depths in the probe (5, 20, and 50 cm). This tube was filled with ground and dry soil. To check the behavior of the sensors directly in soil and to obtain the analytical curves in this environment, 3 mL of the previously described standard solutions was added throughout the inner polyethylene tubes over the sensor sets. The system validation process was carried out altering the initial soil concentrations of both analytes. Thus, additions of a 10% (v/v) H₂SO₄ solution and a CaCl₂ solution were accomplished for pH and Ca membranes evaluation, respectively. During the registered potential variation, several soil samples were collected from the lateral openings, analyzed by the standard methodology, and compared with the results provided by the sensor system. The generated pH results were compared with the standard methodology using two different extraction methods: extraction with CaCl₂, most used in routine soil analysis laboratories, and extraction with water, less recommended but still used in some laboratories.

The time-domain reflectance technique is widely known to measure edaphic water content and soil electrical conductivity (16). In this way, the present work also proposes to investigate the influence of soil moisture on the response of the sensors. Thus, an alternative TDR antenna together with a multivariate calibration model that estimates the existing relation between soil moisture and calcium concentration were used. The variable temperature was kept constant at approximately 20 °C to minimize the influence of this parameter on the responses.

RESULTS AND DISCUSSION

pH. In Figure 1a, one can observe an external calibration of the sensor system with standard solutions covering a pH range from 3 up to 10. The slopes obtained from each analytical curve were as follows: (i) 5 cm, $-45.4(\pm 0.1)$ mV pH⁻¹; (ii) 20 cm, $-42.5(\pm 0.1)$ mV pH⁻¹; and (iii) 50 cm, $-40.4(\pm 0.1)$ mV pH⁻¹. The obtained analytical curves do not differ significantly among depths, but a general sub-Nernstian response was observed. The Nernstian slope was not reached because the applied experimental conditions were different from those usually employed to determine this parameter. Among the causes related to the deviations from ideality due to experimental conditions, it is necessary to take into account first the lack of stirring to ensure uniformity of electrolyte concentration from bulk (soaked cotton) to the electrode surface. In this way, one can fail to recognize that some time is required to bring surface concentrations to bulk values (18). This can cause a fast initial potential change, followed by a monotonic change in the potential to steady-state value that was observed in Figure 1a,b. This drift in the sensor response was also caused by the absence of ionic strength adjustment, which produces a solution resistance smaller as compared with membrane resistance (18). However, despite the non-Nernstian behavior presented by the pH membrane, the analytical applicability of the sensors was not affected at all, once brusque or fast soil pH changes are rare and the proposed sensor system is able to follow the soil pH changes.

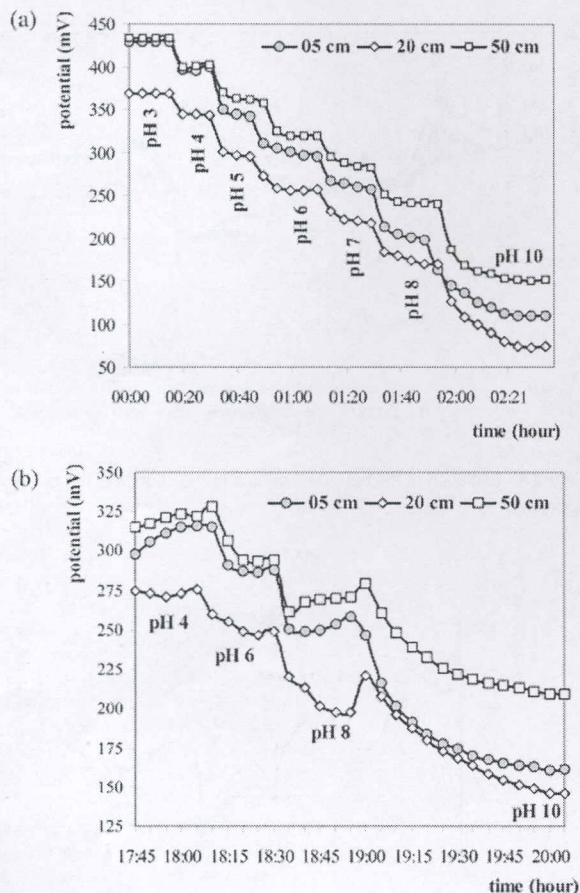


Figure 1. (a) External calibration of the sensors using cottons soaked in buffer solutions. (b) In-soil calibration using buffer solutions added through the polyethylene tubes.

Figure 1b shows a calibration analogous to the previous one with pH standard solutions added through the polyethylene tubes within the soil. A more irregular behavior can be observed as compared to that one presented by the sensors tested outside the soil, which is related directly to soil influence over the pH equilibrium (high buffer capacity). This influence becomes more evident, verifying the sub-Nernstian slopes obtained from analytical curves if compared to that described in the paragraph above: (i) 5 cm, $-29.8(\pm 0.6)$ mV pH⁻¹; (ii) 20 cm, $-29.5(\pm 6.4)$ mV pH⁻¹; and (iii) 50 cm, $-30.4(\pm 7.7)$ mV pH⁻¹. This observed behavior is related to the buffer effect that the soil exerts on the pH variation, an intrinsic characteristic of this kind of matrix due to the presence of organic matter and clay, which act as cation-exchange complexes, as well as due to the presence of soil carbonates. Again, this sub-Nernstian slope did not interfere in the capacity of the probe to successfully monitor the soil pH changes, giving excellent results as observed in the next paragraph.

To evaluate the behavior of the sensor system to pH changes in an extreme condition, 25 mL of a sulfuric acid solution (10% v/v) was added to the soil with the purpose of simulating the correction of a calcareous soil. Figure 2 shows the evolution of the potentials due to the addition of the acid solution. An abrupt change of potential of approximately 130 mV is observed at the 5 cm depth sensor, indicating an increase in the hydrogenionic concentration in that region, or else, a pH decrease. Because of the absence of soil solution mixing, after

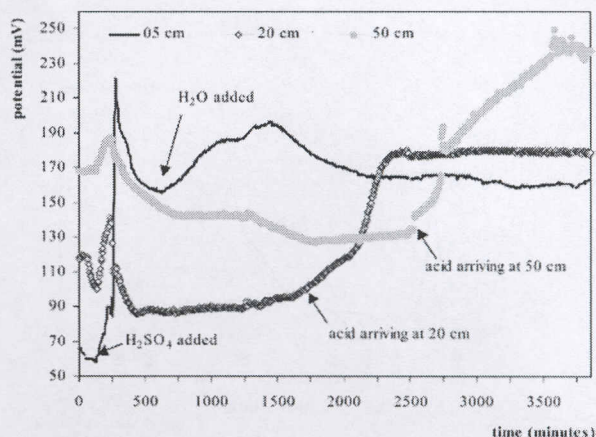


Figure 2. Potential profiles related to soil pH change caused by the acid addition.

the brusque change of potential occurs, the monotonic decreases until the potential fits a steady-state value (after 10 h of experiment). After signal stabilization, water in excess was added over the soil profile to provide the percolation of the excess acid solution. The 5 cm depth sensor indicated a new increase of the potential after water addition, which slowly decreased to a steady-state value of approximately 160 mV. As the initial potential of this sensor was around 70 mV before the addition of acid and assuming an average sensitivity of 30 mV dec⁻¹ for the sensors buried in soil, one could consider that soil pH roughly varied 3 units of pH.

The same process occurs for the sensor installed at a 20 cm depth. One can see an abrupt increase of potential followed by a drop to a constant value. However, this potential is lower than the initial one, characterizing it with a lower H⁺ concentration. This pH increase could be happening due to a strong ionic exchange (basic ions exchanged by H⁺) carried out at the 5 cm depth region. The exchanged ions reach the 20 cm sensor after percolating, lowering the pH. At this point, the potential reaches 90 mV until all excess of the acid solution added and that was not totally depleted at 5 cm reaches the 20 cm region after water addition over the soil profile, increasing the potential and decreasing the pH, as observed in Figure 2 (at around 30 h of experiment). At the 50 cm region also occurs the same sequence of processes described for the 20 cm one; however, they occur more slowly. First, a slow and gradual pH reduction takes place until a stable value is attained, which starts to increase once again at around 40 h of experiment, pointing out the arrival of excess of acid deposited in the top of the column and leached by water addition. If one considers the initial and final potential values for the 20 and 50 cm depth sensors, as well as the average sensitivity of the sensors buried in soil, the variation of pH for both depths was of approximately two units.

Figure 3 presents different potential profiles registered by the sensor system as well as the soil pH analysis (combined glass electrode) using two different extraction methods, extraction with distilled water, and extraction with 0.05 mol L⁻¹ CaCl₂, for the 20 cm depth sensor. A better agreement between sensor results and the extraction procedure was observed with the use of CaCl₂. This effect could be explained due to the high ionic strength presented by the extractor that allows minimizing soluble salts and causing a measured pH inferior to the real one. These results demonstrate that the extraction with CaCl₂ is more efficient, and significant differences between the values provided by the sensor system and the method of comparison

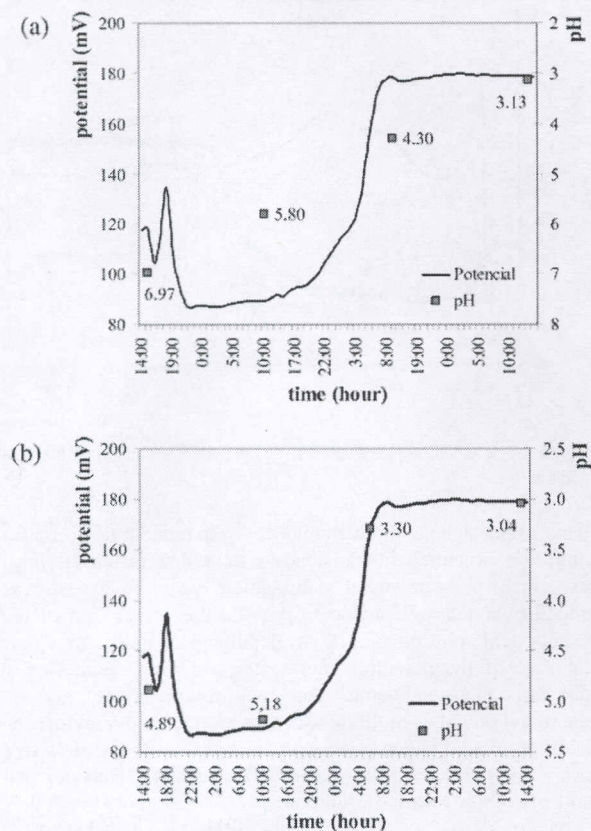


Figure 3. Potential profiles vs comparative soil pH determination method to the 20 cm depth sensor. (a) Extraction with water and (b) extraction with a CaCl₂ solution.

are minimal. These findings were the same for the other depths monitored. The relationships obtained between the potentials given by sensor system and the results obtained by soil standard methodologies show a different behavior observed for sensors located at different depths. The 5 cm depth sensor presented lower sensitivity ($-28.76 \text{ mV pH}^{-1}$, CaCl₂ extraction), whereas the 20 cm depth sensor showed sensitivity and linear work range similar to that observed with the external calibration procedure ($-41.72 \text{ mV pH}^{-1}$, CaCl₂ extraction). On the other hand, 50 cm sensor presented super-Nernstian sensitivity ($-62.64 \text{ mV pH}^{-1}$, CaCl₂ extraction). These facts can be related to the soil buffer capacity, which is different at the various soil depths, being higher at the surface and decreasing as the depth increases, causing a change in sensor sensitivity.

Calcium. Using the same experimental methodology applied in the case of the pH sensor system evaluation, an external calibration of the calcium membranes sensors was carried out using CaCl₂ standard solutions with concentrations ranging from 10^{-5} up to $10^{-1} \text{ mol L}^{-1}$. The slopes obtained from each analytical curve were as follows: (i) 5 cm, $63.9(\pm 2.70) \text{ mV pH}^{-1}$; (ii) 20 cm, $69.5(\pm 9.11) \text{ mV pH}^{-1}$; and (iii) 50 cm, $67.5(\pm 10.9) \text{ mV pH}^{-1}$. From the sensitivity values, one can observe a super-Nernstian behavior attributed to the calibration process. However, the nonexistence of significant differences among membranes showing an equal conditioning process can be seen. Similar results were obtained when the membranes were evaluated inside the soil. This behavior could be occurring due to a characteristic of the membrane, which presents positive deviations of the Nernstian response above concentrations around $10^{-2} \text{ mol L}^{-1}$ and working without sufficient stirring

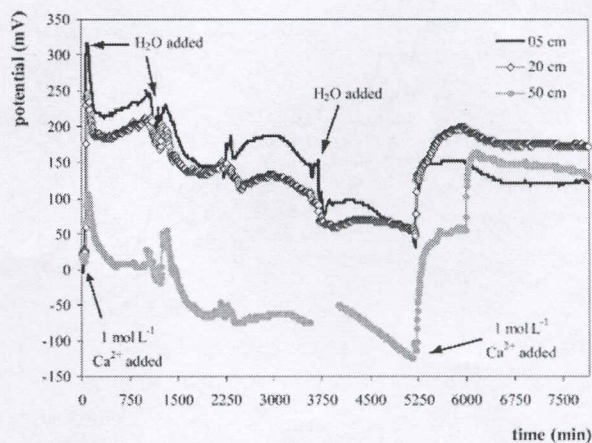


Figure 4. Evolution of the potentials related to the change of the calcium concentration in soil.

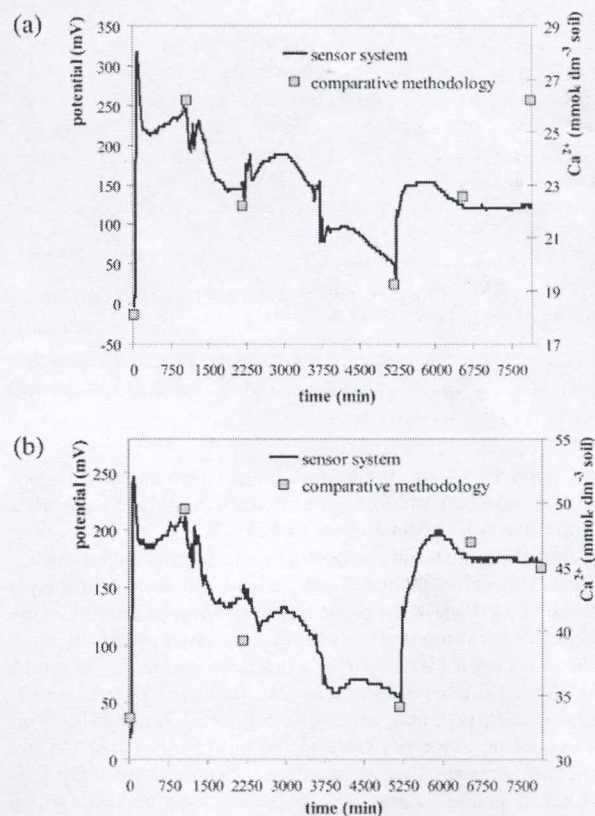


Figure 5. Comparison carried out between the results obtained by the calcium monitoring system (black line) and the comparative soil calcium determination method (gray squares). (a) and (b) Sensors at 5 and 20 cm depth, respectively.

and ionic strength adjustment. These high-activity deviations occur by failure of Donnan exclusion (18). It is also known that at ideal conditions of measurement, liquid-ion exchangers in solutions of a single permselective ion (e.g., Ca²⁺ bathing solutions and a calcium organophosphonate ion exchanger) can respond rapidly to activity changes of calcium on one side of the membrane (18). For these Ca membranes, a Nernstian slope was obtained in the range of 10^{-4} up to $10^{-3} \text{ mol L}^{-1}$. However, when measured in the range of 10^{-3} up to $10^{-1} \text{ mol L}^{-1}$, the

Table 1. Linear Equations Obtained Relating Sensor Probe Response and Calcium Analysis Standard Methodology Results

| depth (cm) | equation | r ² |
|------------|--|----------------|
| 5 | $E_{(mV)}^a = 29.6(\pm 1.4)^b \times [Ca_{FAAS}]^d - 531.4(\pm 6.2)^c$ | 0.9779 |
| 20 | $E_{(mV)} = 10.3(\pm 0.9) \times [Ca_{FAAS}] - 295.1(\pm 4.1)$ | 0.9129 |
| 50 | $E_{(mV)} = 11.5(\pm 1.2) \times [Ca_{FAAS}] - 373.8(\pm 4.3)$ | 0.9778 |

^a $E_{(mV)}$ = potential. ^b Errors obtained with a 95% confidence level for S_a . ^c Errors obtained with a 95% confidence level for S_b . ^d FAAS (mmol Ca dm⁻³ of soil).

slopes obtained presented a super-Nernstian behavior as described above. Thus, this associated phenomena—nonideal calibration process and fast response of the membrane—caused this unexpected behavior of the calcium membranes. Nevertheless, as stated above for pH membranes, these slopes did not diminish the probe capacity to successfully monitor the soil Ca changes, as seen for the result described in the following.

Once the external calibration and the membrane conditioning were finished, the sensor system was evaluated, trying to simulate real soil conditions and allowing samples collection to validate the system for comparison with the standard methodologies. In **Figure 4**, the behavior of the sensor system is shown after two calcium additions in the soil. Initially, the sensors presented constant potential values. After the addition of 10 mL of a 1.0 mol L⁻¹ CaCl₂ solution, three very similar profiles are observed. A strong influence of the sudden change of the soil ionic strength was observed, which was detected by all of the sensors. At 5 and 20 cm depths, an abrupt potential increase was observed, followed by a decrease to a higher potential, showing an evident increase in the Ca²⁺ concentration at this soil section. However, at the 50 cm sensor depth, the potential returned to the initial potential, showing that after the rapid membrane response to change of ionic strength, the real potential of the sensor is attained. After the first addition of calcium, various successive additions of water in excess were carried out to force the percolation of the ion to the 50 cm region. At the first 20 cm depth, the water added caused a decrease in the potential, pointing to a gradual decrease of the calcium concentration. However, at the 50 cm depth sensor, the potential also decreases, showing that the calcium percolation is slow and moisture-dependent. The arrival of calcium at the 50 cm depth is observed only after the second addition of a 10 mL aliquot of a 1.0 mol L⁻¹ CaCl₂ solution over the soil profile.

Figure 5 shows the potential profiles for 5 and 20 cm depths sensors with punctual soil collections for standard analyses by comparison. From this figure, one can see a good correlation between both methodologies. **Table 1** shows the relationships obtained between the potentials given by the sensor system and the results obtained by standard soil methodologies. The equations presented a similar sensitivity for the 20 and 50 cm sensors, whereas the 5 cm sensor did not. This fact is explained by the difference of soil moisture between depths determined by TDR. The values of soil moisture determined for the studied depths were as follows: among 14–18% for the 5 cm sensor, among 21–24% for the 20 cm sensor, and among 20–26% for the 50 cm sensor. For low values of soil moisture, the sensor presents a more sensitive response—almost three times more—to the variation of the calcium concentration as compared to the same behavior when values of moisture are higher. This difference is related to a characteristic of potentiometric sensors, which measures calcium activity in the edaphic water that is different among depths. The values of soil moisture were

determined in the time of sample collecting, always around 24 h after addition of calcium solutions or water on the soil surface.

In accordance with the results that characterize the sensor responses in soil, a calibration model was built, allowing determination of the soil calcium concentration starting from the values of potential and soil moisture generated by the sensor system. Multiple linear regression was used, which employed a group of 20 potential and moisture data with the real calcium concentration determined by the comparison methodology. With this developed methodology, the calibration model is represented with the following equation:

$$[Ca^{2+}] \text{ (mmol}_c \text{ dm}^{-3} \text{ soil)} = -2.71(\pm 1.43) + 0.09(\pm 0.01)\text{mV} + 1.61(\pm 0.32)\epsilon$$

This method provides a correlation coefficient of $R^2 = 0.8146$ and a root square mean error of prediction of 5.627. Observing the values of the regression coefficients of the model as well as their deviations, an adequate correlation between both methodologies is shown, allowing a semiquantitative calcium determination in soils.

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