COMPATIBILITY ANALYSIS OF THE SOIL CALCIUM CONTENT BY MULTIFREQUENCY EC SENSORS

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ABSTRACT

Nowadays in precision agriculture, the on-the-go measurement of soil nutrients is an important research topic in the sustainable nutrient management practices. Determining the nutrient content of soils and the judicious and site-specific replacement of missing mineral compounds of soil has a major impact on production costs in terms of current fertilizer prices. Soil sensors currently on the market can only determine total soil salinity. Therefore, selective soil salinity testing is only possible using laboratory methods. However, these methods are rather expensive, slow, and cumbersome. Growers often need faster and cheaper soil sampling process and immediate results. We believe that by developing measurement models of soil sensors, the data delivery process could be significantly shortened, so that measurement results could be processed and used even in real time. In this paper, we prove that electrical conductivity measurements can be a suitable tool for the determination of the selective salinity of soil. In our experiments, the calcium cation content of soil was measured by conductometry in laboratory conditions. In our model, we investigated the effect of a reasonable and well-considered variation of the measuring current frequency on the measurement output variable, i.e. the electrical conductivity (often abbreviated as EC) value. Our experiments have shown that with multi-frequency, solutions containing predetermined concentrations of Ca²⁺ ions, the EC obtained as an output parameter follows different functions.

1. INTRODUCTION

1.1. COMPOSITION OF MINERALS IN SOIL SOLUTION AND THE HYDRATED SHELLS

Effective agricultural soil management should consider the structural, biological, and mineral aspects of soil health, extending beyond the focus on nitrogen (N), phosphorus (P), and potassium (K), to ensure the production of...
The soil moisture contains a diverse array of inorganic salts, organic matter, and gases. Mineral salts that dissolve in the soil are dissociated into ions carrying positive and negative charges, each surrounded by a hydrate shell. The predominant ions found in the soil solution include:

- \( \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+, \text{NH}_4^+ \) and in some soils \( \text{Al}^{3+}, \text{Fe}^{3+} \) or \( \text{Fe}^{2+} \) (as cations)
- \( \text{HCO}_3^-, \text{CO}_3^{2-}, \text{Cl}^-, \text{SO}_4^{2-}, \text{NO}_3^-, \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-} \) (as anions).

Most dissolved organic compounds in soil comprise organic acids and low-molecular-weight humic substances, with the most notable dissolved gases being \( \text{CO}_2 \) and \( \text{O}_2 \). Soluble substances in the soil primarily result from weathering and soil formation processes. Partial root contact with soil particles and the soil solution limits the effective absorption of nutrients by plant roots. Furthermore, the soil texture plays a significant role in determining the soil’s capacity to retain air, water, and nutrients. The application of fertilizers and compounds in irrigation water in agricultural regions can alter the soil's salinity. The exploration of the interaction between solvated ions and water has garnered significant attention due to its pivotal role in diverse chemical, biological, and environmental processes.

Figure 1 illustrates the size of the hydrate shell in aqueous solution. The thickness of the hydrate sphere in the solution is influenced by the diameter of the dehydrated cation and its charge. Generally, the smaller the diameter of the dehydrated cation and the higher its charge, the thicker the hydrate sphere in the aqueous solution. This characteristic also impacts the mobility of hydrated ions. Notably, potassium stands out as the most mobile element in the soil, making it readily available to plants. However, caution is necessary to prevent its leaching from the vadose zone of the soil due to its high mobility.

**Figure 1** The Dimensions of the Aqueous Hydrate Envelope for Each Element in the Soil, As Outlined by Stefanovits et al. (2005)
Indeed, the common cations found in soil exhibit a broad spectrum of sizes, as depicted in Figure 2. Research by Rengasamy (1998) demonstrated that the dispersive impact of Na surpasses that of K, while the flocculating effect of Ca is more pronounced than that of Mg. Traditionally, these cations have been referred to as base or base-forming cations Rengasamy (2016). The hydrated radii of these cations play a crucial role in shaping the composition of soil.

**Figure 2**

![Ionic and Hydrated Radii for Common Ions](attachment:image.png)

Figure 2 The Ionic and Hydrated Radii, Expressed in Angstroms, For Certain Common Ions are Detailed in Research Conducted by Luo et al. (2019).

### 1.2. ASSESSING SOIL NUTRIENT PROPERTIES THROUGH THE SOIL SENSORS

In the realm of crop production sensor measurements, various sensor categories are employed, including crop sensors, environment sensors, function monitoring sensors, and soil sensors. In investigating the trend of sensor-based solutions, it becomes evident that the future of site-specific crop production is evolving towards a sensor-centric approach. This shift is driven by the ongoing challenge in precision agriculture—swift and cost-effective acquisition of crucial soil characteristics Hajdú (2018).

Nowadays, sensor technology stands out as one of the rapidly advancing domains in precision agriculture. A soil sensor, for instance, serves as a tool capable of identifying alterations in the physical or chemical characteristics of the soil, translating them into electrical signals, electric currents, and voltages. Precision agriculture hinges on the continuous monitoring of soil conditions through the integration of information technology and GPS technology Mandal et al. (2021). Subsequently, the gathered data is analysed to manage the spatial-temporal variations in both soil and field crops. Gathering, processing, and analyzing data are essential elements of precision agriculture, which seeks to enhance agricultural productivity Kukadiya and Meva (2023). In the future the evolution of sophisticated, intelligent AI algorithms that possess the capability to learn, adapt, and potentially take autonomous actions, as opposed to merely adhering to predetermined instructions, marks a pivotal moment for innovators and technology providers Trisal & Mandloi (2021). This valuable information guides decisions regarding the specific application of crop inputs, encompassing the judicious use of water and fertilizers. The adoption of such technology holds the potential to enhance efficiency.
Calcium plays a major role in developing the strength of the cell wall, helping to record potassium, phosphorus, and nitrogen. It reduces sodium uptake, thereby increasing the salt tolerance of the plant, which is an advantage for saline soils. It is essential for root growth, which without calcium does not grow but dies. The escalating costs of fertilizer and growing environmental concerns related to chemical run-off into drinking water sources have propelled precision agriculture and site-specific management to the forefront of contemporary technological advancements in agriculture and ecology. With the rising expenses of fertilizer production inputs, notably nitrate (N), phosphate (P), and potassium (K), those involved in agriculture seek ways to optimize plant yield while minimizing the application and consumption of fertilizers. Given that these macro-nutrients exhibit variations even on a small scale within a cultivated field, numerous researchers have endeavored to create an on-the-go sensing device capable of mapping the presence of these chemicals in situ. This map, when overlaid with parameters like pH, electrical conductivity (EC), crop yield, and soil mechanical properties, can provide a precise prescription for fertilizer application that varies spatially Sinfield et al. (2010).

In 2020, the global Agricultural Sensors market achieved a valuation of USD 1,505.4 million, and it is projected to attain USD 3,200.8 million by 2028, demonstrating a Compound Annual Growth Rate (CAGR) of 11.04%. Smart Sensors empower farmers to optimize yields while minimizing resource usage, including fertilizer, water, and seeds. Through the integration of sensors and field mapping, farmers can effectively manage their crops at a micro-scale, conserving resources and mitigating environmental impacts. The roots of smart agriculture trace back to the 1980s when Global Positioning System (GPS) capabilities became available for civilian use. The accurate mapping of crop fields enabled farmers to monitor and apply fertilizer and weed treatments precisely where needed. In the 1990s, early adopters of precision agriculture utilized crop yield monitoring to generate recommendations for fertilizer and pH corrections. As technological advancements allowed for more variables to be considered in crop models, more accurate suggestions for fertilizer application, irrigation, and optimal yield harvesting became possible ICT - Agricultural Sensors Market. (2022).

Numerous researchers and manufacturers are actively working on on-the-go soil sensors designed to directly assess the mechanical, physical, and chemical properties of the soil. While these widely adopted ground sensors may be less precise compared to individual sampling and laboratory tests, their practical advantage lies in their rapid measurement capabilities, making them a more economical choice in practice Hajdú (2018). In the times ahead, there will be widespread access to faster and more cost-effective measurement tools for mechanized soil testing and nutrient mapping solutions. Achieving sustainable agricultural and environmental management requires a deeper comprehension of soil characteristics at increasingly precise scales. Traditional methods like soil sampling and laboratory analyses, being slow and expensive, fall short in delivering this essential information Adamchuk & Rossel (2010).

Proximity detection is characterized by the utilization of sensors deployed in the field to capture signals from the ground, where the sensor unit is either in direct contact with or close to the ground (within 2 m), as defined by Viscarra Rossel et al. (2011). In practical terms, the following measurement principles and sensors are differentiated, as outlined by Grunwald et al. (2015):
• Electrical Conductivity Sensors (EC)
• Ground Penetrating Radar and Reflectometers
• VIS-NIR-MIR Diffuse Reflectance Sensors
• Magnetic Susceptibility Sensors
• Gamma-Ray sensors
• X-ray Sensors
• Additional Proximal Soil Sensors, such as photoacoustic spectroscopy, laser-induced breakdown spectroscopy, laser-induced fluorescence spectroscopy, and inelastic neutron scattering, are available. Mechanical sensors gauging soil penetration resistance have been widely employed and integrated into soil science and precision agriculture alongside other sensors. These applications span from assessing soil compaction to creating 3D models of soil layers.

Certainly, the various sensors can be combined as needed, termed as a multisensory measurement.

1.3. CONDUCTOMETRY IN SOIL SENSOR TECHNOLOGY

Soil characteristics often exhibit substantial variation within a field, posing a challenge in precision agriculture where acquiring sufficient soil data is crucial for accurately understanding this variability. Soil electrical conductivity (EC) has emerged as a widely adopted tool for mapping soil diversity within fields, with correlations typically established with soil texture, moisture, and salinity. Soil texture, being a critical factor in crop yields, influences water-holding capacity, cation-exchange capacity, rooting depths, drainage, and other properties impacting crop production Lund (2008).

Electrical conductivity characterizes the good conductance of components. Conductometry, an analytical method, is based on measuring the electrical conductivity of solutions. In analytical chemistry, the measurement of electrical conductivity in electrolyte solutions provides analytical information, with insights derived from changes due to chemical reactions. The conductivity of materials (denoted as \(G\), with the unit in siemens, S) is the reciprocal of their electrical (ohmic) resistance (denoted as \(R\), with the unit in ohms, \(\Omega\)). Electric conduction necessitates the presence of charge carriers (e.g., electrons or anions and cations) capable of movement under the influence of an electric field. Ion migration in the solution due to the electric field facilitates the electrical conduction of solutions. This underlies the distinction between electrical conductors and insulators.

Pure (distilled) water, containing minimal charge carriers at a concentration \([H^+] = [OH^-] \approx 10^{-7}\) mol L\(^{-1}\) corresponding to autoproteolysis, conducts electricity to a negligible extent, rendering it essentially an insulator. However, the concentration of cations and anions in aqueous solutions of electrolytes can be significant, rendering them conductive based on the degree of electrolytic dissociation. Each ion in the solution contributes to the conduction value, and while these contributions are inseparable, conductometry is not suited for the selective measurement of individual ions, making it a non-ion-specific method Galbács et al. (2015).

- Consequently, its analytical application is limited to systems that either contain only a single electrolyte (where the "background" contribution is negligible)
or undergo chemical reactions altering the mobility of ions, significantly deviating from a non-zero "background" Galbács et al. (2015).

The global issue of soil salinization poses a significant threat to land productivity Hossain (2019). Saline soils have been identified in over 100 countries, covering more than 1,125 million hectares of land Wicke et al. (2011). With an annual increase of approximately 1–2%, it is estimated that by 2050, soil salinity could affect 50% of available arable lands, posing a serious challenge to the sustainable development of global agriculture Massoud (1981).

The measurement of electrical conductivity stands out as a crucial in-situ tool for soil testing essential in precision farming practice. Consequently, a substantial body of literature focuses on the development of EC detectors. These detectors typically employ a traditional four-electrode configuration Li et al. (2006), Seifi et al. (2010), Pei et al. (2012). The conventional current-voltage four-electrode method is designed for in-situ measurements, aiming to develop an affordable, user-friendly, and precise in-situ soil EC detector with integrated control and data processing procedures Seifi et al. (2010). Apparent soil electrical conductivity, derived through this method, serves as a simple and cost-effective means of obtaining valuable information about soil characteristics crucial for precision agriculture Seifi et al. (2010).

This paper aims to present fundamental research on measuring the selective calcium content of soil through multifrequency electrical conductivity measurements based on conductometry principles as is EC measurement. This basic research within the framework of the Hungarian University of Agriculture and Life Sciences, Institute of Technology soil sensor research project, focuses on methodological advancements to replace slower, more complex, and relatively expensive laboratory determinations of salinity with as many on-the-go measurements as possible. It is important to note that, to the best of current knowledge, conductivity tests using soil sensors alone may not be sufficient to infer the salinity properties of a given field. The measurement is influenced by factors such as the uneven distribution of nutrients, varying pH conditions, diverse particle compositions, differences in organic matter content, and even temperature fluctuations Corwin & Lesch (2005).

2. METHODS AND MATERIALS

2.1. SPECIFICATIONS

2.1.1. SOLUTIONS

The experiments took place at the Institute of Technology laboratory within the Hungarian University of Agriculture and Life Sciences, maintaining a constant temperature of 22 °C. Both solutions and soil were subjected to measurements under these conditions.

The objective of the study was to investigate the impact of cations from dissolved salts in soil moisture under natural conditions. Calcium ions (Ca²⁺) were selected for examination due to the pressing and costly concern of judiciously replacing Ca²⁺ microelements in cultivated plants. To introduce these ions into the soil solution, water-soluble salts were utilized, specifically the chloride salts of the Ca²⁺ cation. For the experiment, 1 M concentration (1 M = 1 mol dm⁻³) stock solutions were prepared from Calcium chloride (CaCl₂), 99.0 - 103.0%, CAS: 10043-52-4. These solutions underwent further dilution using a series of concentrations: 1 M; 0.66 M; 0.33 M, and distilled water, where 0 M served as the reference measurement. To prevent measurement errors, the system was consistently rinsed with distilled water.
water between measurements, ensuring any residual ions on the electrode from the prior measurement did not influence the subsequent results.

### 2.1.2. SOIL

For our research, the soil sample were taken with pH\textsubscript{H_{2}O} < 7 and undetectable CaCO\textsubscript{3} content from Szárítópusta, Gödöllő, from 0-20 cm layers of arable land (47°35’ 47.65” N, 19°21’ 18.54” E). According to the classification of the IUSS working group WRB, 2015, the soil type was identified as Eutrict Arenosol (Aeolic, Aric, Ochric, Raptic) soil at 232 m altitude, characterized by a sandy texture.

### 2.1.3. HARDWARE FOR MEASUREMENT CIRCLE

Components of the measurement circuit, as illustrated in Figure 3, include:

1. SOURCETRONIC ST2829C Precision LCR meter with USB memory stick.
2. SOURCETRONIC ST26011B Test Fixture: The instrument features a resolution of 0.00001 nS and a basic accuracy of 0.05%. The voltage applied to the electrodes during measurement is 10 V DC, and the instrument’s output impedance is 100 Ω.
3. KSP-F01A Dosing Pump.
4. Measuring cup (500 ml, 50 ml increments) utilized for storing the input solution.
5. Measuring cylinder with dimensions of Ø 61 mm x 137 mm.
6. Two measuring electrodes with Ø 2 mm, a length of 80 mm (full length insulated, uninsulated part length 5 mm), a probe distance of 12 mm, made of stainless steel.
7. Piping with an inner diameter of Ø 3 mm.
8. Tray with a raiser.

![Figure 3 The Measurement Circuit](image)

### 2.2. THE MEASUREMENT PROCEDURE

The precision LCR meter conducted measurements, registering electrical conductivity between two stainless steel electrodes immersed in predefined soil
solutions following a predetermined program frequency. After completing the measurement sequence, the system initiated a continuous cycle, restarting the measurement process endlessly. Frequency values employed for the measurements were documented within the range of 20 Hz to 10^6 Hz.

Each new measurement cycle commenced with the calibration of the peristaltic pump, ensuring a liquid delivery rate of 0.5 g s\(^{-1}\). Throughout the measurements, the pump at the bottom of the measuring cylinder propelled the liquid solution into the cylinder (refer to Figure 4). The solution was introduced into the cylinder through a 3D-printed distribution plug, ensuring uniform saturation of the soil within the cylinder. Exiting the measuring cylinder through perforations at the top, the solution collected on the tray beneath, facilitating the continuous removal of used output liquid.

Figure 4

Prior to initiating each new measurement, the soil pastes in the measuring cylinder underwent rinsing with distilled water. This precautionary step aimed to prevent any influence from ions lingering from the preceding measurement on the current results. The experiments were iterated three times for each mixed input solution, involving the addition of 300 ml of the input solution in each instance, followed by neutralization using 300 ml of distilled water. If the electrical conductivity of the soil paste remained above 0.1 mS during washing, an additional rinse with 100 ml of distilled water was conducted. Each measurement was replicated three times.

3. RESULTS AND DISCUSSIONS

3.1. THE BEHAVIOUR OF CALCIUM SOLUTIONS IN SOIL

Based on the measurements with Calcium chloride solutions of different concentrations, the arithmetic mean of the measured electrical conductivity (EC) values was calculated for each concentration and frequency. This was done by examining the adjacent values and averaging them if the variation did not exceed 5 % (\(\Delta < 5 \%\)). Consequently, frequency-dependent averages were obtained for the overall measurement. Then, after performing the necessary calculations, the measurement results of the calculated data series per ion, per concentration and per measurement frequency were recorded. The result of the measurement is shown in Figure 5.
It should be observed that:

- The distilled water (0M), representing the reference data series, is not visible due to its nearly zero values.
- The measurement at 5 kHz frequency is flawed, evident from the extent of scatter in the data.
- The measured values were evaluated for measurement reliability using the standard deviation of the mean estimate as shown in Figure 5.

It was evaluated that by plotting the variations of the electrical conductivity (EC) of the tested concentrations on a logarithmic scale, we can better elucidate the different behaviour of the solutions. Figure 6 not only illustrates the correlation between increasing concentration and increasing EC, but also highlights that as the measurement frequency increases, the measured EC value also increases.

Figure 5

**Figure 5** Electrical Conductivity (EC) Values for Various Concentrations of CaCl2 Solutions, Along with Standard Deviation

![Figure 5](image)

Figure 6

**Figure 6** Electrical Conductivity (EC) Values for Varied Concentrations of CaCl2 Solutions Across Logarithmic Frequency Scales.
Representing the measurements in a 3D space provides a more pronounced illustration of the behavior of the solutions, as depicted in the ensuing diagrams in Figure 7.

**Figure 7**

![Figure 7 Electrical Conductivity (EC) Portrayed in Relation to Ca2+ Concentration and Frequency](image)

Ultimately, by graphing the frequency on a linear scale and plotting the EC measurement outcomes for solutions of varied concentrations, fitting a function to the acquired points was performed, with a consideration that $R^2 > 0.9$. The reference functions for the diverse Ca$^{2+}$ cation concentrations are delineated in Figure 8.

**Figure 8**

![Figure 8 EC Saturation Curve for Solutions with Different Ca2+ Concentrations](image)

The reference functions for the calcium (Ca$^{2+}$) cation in the established measurement model are as follows, demonstrating a highly accurate fit:

- 1M solution: $f(x) = 5.782x^{0.121}$, $R^2=0.9753$
• 0.66M solution: \( f(x) = 4.1613x^{0.0858}, R^2=0.9919 \)
• 0.33M solution: \( f(x) = 5.0884x^{0.066}, R^2=0.991 \)
• 0M solution as is distilled water: \( f(x) = 5E - 09x + 0.0035, R^2=0.9307 \)

4. CONCLUSION

As soil sensors become more widespread, on-the-fly measurement of important soil properties such as nutrient content will allow farmers to get immediate information on the condition of the soil as the most important resource for production. This measurement method not only saves resources, but also minimises environmental impact through the judicious and site-specific application of nutrients. The use of soil sensors facilitates rapid, real-time, and cost-effective soil testing and nutrient mapping solutions Trosin et al. (2021), Khan et al. (2021).

In the present study, we sought to answer whether one of the simplest, most economical, and widely used measurement methods - a novel approach to measuring electrical conductivity - could provide an opportunity for selective laboratory measurement of soil salinity. Our experiments showed a significant correlation between the relative concentration of Ca\(^{2+}\) in soil, the measurement frequency, and the measured electrical conductivity (EC). As the measurement frequency increased, the measured EC of CaCl\(_2\)-saturated soil varied according to the functions detailed in the results and increased with increasing frequency in a manner that could be described by functions.

In the future, our aim is to develop a mathematical model that can be used to guide the estimation of the selective salinity of soil under laboratory conditions using the conductometric method. An interpolation model based on regression functions of reference values shows that by systematically varying the measurement frequencies, the selective salinity of a known soil can be determined by EC measurements under laboratory conditions. For solutions with identical Ca\(^{2+}\) ion concentrations, EC saturates according to different functions depending on the measurement frequency.

CONFLICT OF INTERESTS

None.

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