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## Views &amp; Comments

## The War for Fertile Soil: Advancements in Soil Nutrient Field Sensors

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## 1. Introduction

Soil is the foundation of agriculture and of life itself [1], and fertile soil gives birth to crops with rich nutrients. Crops have significant species-specific demands for soil nutrients, including nitrogen (N), phosphorus (P), potassium (K), trace elements, and so forth. Differences in crop nutrient needs are mainly due to the physiological characteristics of the development of different organs and the diversity of metabolic pathways. For example, leafy crops (spinach, lettuce, etc.) require more N for stem and leaf growth, while fruit crops (tomatoes, peppers, soybeans, etc.) rely on more P and K to facilitate the formation of organs such as seeds and fruits. Cereal crops (corn, wheat, etc.) have a prominent demand for N and silicon (Si), which are used for protein synthesis and to increase stem strength, while fruit trees are sensitive to trace elements such as calcium (Ca) and magnesium (Mg), which are used to stabilize cell walls and promote photosynthesis. It can thus be seen that refined and intelligent management of soil nutrition is crucial for crop growth. Since the invention of chemical fertilizers, hailed as one of the greatest achievements of the Industrial Revolution, farmers have been able to intervene very specifically in soil nutrition. That said, while chemical fertilizers have brought about a significant increase in yield, their misuse poses a serious threat to the environment and to underground drinking water [2].

Despite the self-evident importance of soil nutrients, it is not possible to rapidly measure them onsite; instead, a complex process must be followed, from field sampling to laboratory analysis. This time-consuming measurement process makes it difficult to classify soil nutrient levels and implement variable-rate fertilization in real time. Although precision agriculture and smart agriculture are already developed rapidly, the unknown real-time state of soil nutrients requires farmers to apply fertilizer relatively blindly, preventing the achievement of true precision agriculture.

Soil nutrients are challenging to identify for two main reasons. First, they exhibit significant diversity, with different parameters having entirely different implications for different crops. For example, the soil in a crop field typically contains a large amount of N, the vast majority of which is in organic forms. Only a small fraction

of this N—such as nitrate nitrogen ( $\text{NO}_3^-$ -N) and ammonium nitrogen ( $\text{NH}_4^+$ -N)—can be directly absorbed by the crops. However, although organic N is not directly absorbable by crops, it can be continuously transformed into readily available N and is thus used as an important indicator to assess the soil's inherent fertility. Second, the soil matrix is extremely complex, with dozens of distinctly different soil types across the world. Even within the same region and for the same type of soil, there can be significant variations in moisture content, physical form, texture, and particle size in a field. Therefore, the onsite identification of soil nutrients is regarded as one of the most challenging problems in soil nutrition [2].

The development of soil nutrient sensors holds both challenges and opportunities. A breakthrough in this field could revolutionize agricultural production, bring about transformative technological progress, and enable true precision farming. Thus, the scientific community's exploration of soil nutrient sensing technology has been relentless. Particularly over the past two decades, with the rapid advancement of materials science, sensor technology, and artificial intelligence, an increasing number of innovative methods have been employed in the exploration of various types of onsite soil nutrient sensing, as shown in Fig. 1, which is on the cusp of significant scientific and technological breakthroughs.

## 2. Current status and challenges of soil nutrient field sensors

## 2.1. Onsite colorimetric and electrochemical sensors: a convenient laboratory in the field

Exploration of the rapid onsite measurement of soil nutrients initially began with the simplification of laboratory methods. The idea was that simplifying complex laboratory analysis methods and instruments such that they could be brought to the field would allow the nutrient status of soil to be obtained onsite. This remains the most widely used detection method at present [3]. The simplification process often occurs in two aspects. First, the pretreatment process is simplified; for example, by making it possible to collect soil in a suitable state, directly add solid extractants in the field, and filter the mixture. Newly developed extractants can even achieve the joint extraction of multiple nutrients. Second, the detection method is simplified; for example, portable multi-band colorimetric sensors have been developed and calibration solutions have been configured to achieve measurement in the field. These methods have been commercially available since the last century

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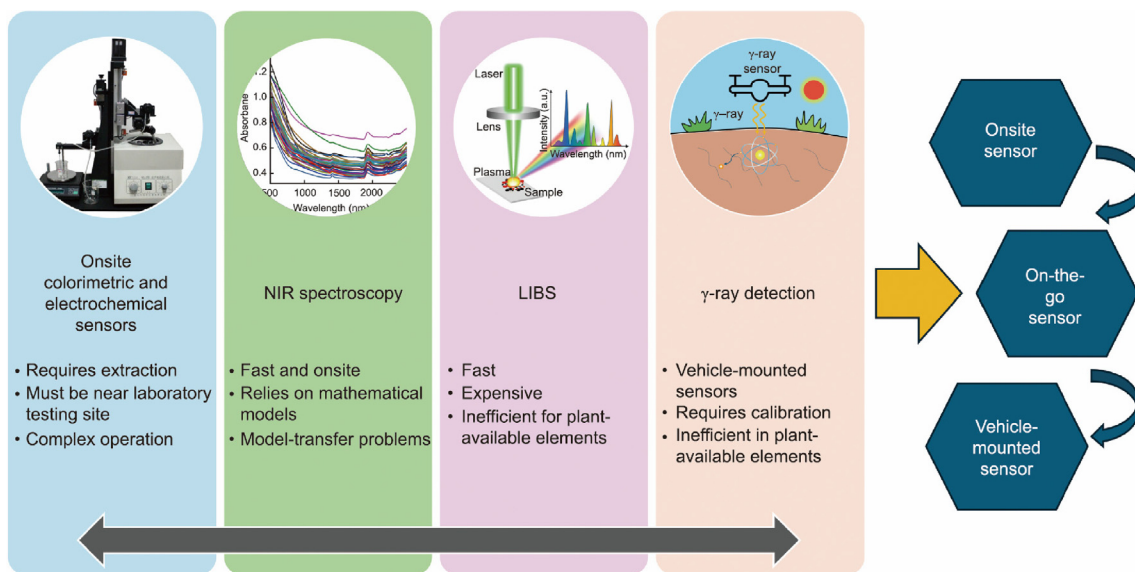


Fig. 1. Current status and challenges of soil nutrient field sensors. NIR: near-infrared.

and are continuously being improved. Skilled operators can measure the content of soil nutrients such as  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and available P within 1–2 h under field conditions.

In recent years, the demand for miniaturized and intelligent equipment has promoted the further development of colorimetric sensors, and smartphone-driven miniaturized  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N, and nitrite ( $\text{NO}_2^-$ ) colorimetric sensors have attracted much attention. Paper-based chips and microfluidic chips have also greatly promoted the field application of colorimetric sensors. In particular, paper-based colorimetric sensors have the advantages of low cost, portability, and easy operation, and they are effective in the semi-quantitative analysis of soil nutrients [4]. However, the drawbacks of onsite colorimetric sensors are also apparent. These sensors require substantial inputs of reagents, including extractants, color-developing agents, and standard solutions, while reagents from different manufacturers vary widely in their quality and purity, leading to significant discrepancies in measurement results. In addition, the complex measurement process can result in considerable operational errors, with well-trained personnel exhibiting significant differences in operations such as extraction and reagent preparation [5].

Electrochemical sensors are excellent tools for simplifying this process and reducing variability [6]. In theory, the uniform preparation of electrodes avoids the differences caused by human factors and reagents. In particular, ion-selective electrodes (ISEs) are suitable for the onsite quantitative analysis of soil nutrients due to their simple circuits, low-cost manufacturing, low maintenance, and highly specific response characteristics. Researchers have developed a series of electrochemical sensors for measuring soil nutrients such as N, P, and K, with detection limits of up to  $10^{-6}$  to  $10^{-5}$   $\text{mol}\cdot\text{L}^{-1}$ . At the same time, surface-modified electrodes make electrochemical sensors more sensitive and selective. However, in practice, the application of ISEs in soil testing is quite rare, for two reasons: First, the components of soil extracts are very complex, exacerbating the already serious cross-sensitivity of IESs. For example, electrochemical electrodes of  $\text{NO}_3^-$ -N are easily interfered with by K ions. Second, the persistent issues of baseline drift and poisoning make sensors suitable as one-time measurement tools but difficult to maintain and use for long-term and multiple applications. Ultimately, electrochemical sensors for soil still rely on prior extraction, and the time for detection depends on the extraction and pretreatment process. Therefore, an important

research focus is on how to shorten the traditional extraction time by using new types of extractants and equipment methods under field conditions [7].

## 2.2. Near-infrared (NIR) spectroscopy: the dance on data

Different molecules exhibit distinct fingerprint characteristics in the NIR region, making NIR spectroscopy a quantitative analytical tool. As early as in the 1980 s, scholars began using NIR spectroscopy to rapidly measure soil nutrients and water content. After decades of development, over 2000 research articles have been published on this topic, most of which are based on diffuse reflectance spectra in the 800–2500 nm wavelength range [8]. The use of diffuse reflectance spectroscopy for soil measurement is extremely simple; minimal soil processing is required, and even the direct measurement of natural, untreated soil is possible. The instruments used have evolved from complex, bulky, and expensive lab-based fourier-transform infrared (FTIR) systems to miniature, low-cost spectrometers. Studies have also reported ways to simplify the spectrometer by using a multiband light source close to the absorption characteristics of the soil samples being tested or by using filters to capture spectral responses from the tested soil samples at specific wavelengths. In recent years, commercial soil sensors based on NIR spectroscopy have also emerged, such as Soil-Care, which is based on a miniaturized FTIR spectrometer, and Veris, which is mounted on agricultural machinery. In addition, the Agrocare nutrient scanner, the Agilent 4300 handheld FTIR spectrometer, and the FieldSpec 4.0 by Malvern Panalytical Ltd. (UK) are relatively mature NIR soil composition measurement sensors.

Nevertheless, despite this extensive research, the challenge of soil nutrient NIR spectroscopy sensing technology remains immense [9]. NIR spectroscopy is inherently vague, as almost no substances exhibit significant absorption peaks in the NIR range; this results in an envelope-like NIR spectrum that must be interpreted using chemometrics and machine learning. Consequently, the optimal subjects of NIR spectroscopy are materials with uniform composition in industrial processes. In contrast, soils vary greatly, with different regions presenting distinctly different physical properties and chemical compositions. Thus, users of NIR sensors often find that models established after considerable effort in sample collection and testing become ineffective when transferred

to another region or farm; in fact, it is even difficult to transfer models to the following year, even if the farm has not changed.

### 2.3. Laser-induced breakdown spectroscopy (LIBS): from Mars to farmland

National Aeronautics and Space Administration (NASA)'s Mars rovers utilize intense lasers to induce plasma emission spectra from Martian rocks in order to measure their composition [10]. Inspired by this, researchers have explored LIBS for soil composition measurement [11]. In LIBS soil detection, the laser directly ablates the soil surface and can simultaneously achieve the high-sensitivity measurement of multiple nutrients (K, carbon (C), Si, Ca, and Mg). Miniaturized and portable LIBS systems are considered one of the best approaches for on-field nutrient quantification. Handheld LIBS has been used to determine the total amounts of the soil nutrients Ca, K, Mg, manganese (Mn), and iron (Fe), with a detection limit reaching  $10^{-6}$  to  $10^{-4}$  mg·kg<sup>-1</sup> [12]. Commercially available LIBS devices for soil measurement also exist, such as the Z-903 handheld LIBS from SciAps (USA) and the Niton Apollo handheld LIBS from Thermo Fisher Scientific (USA). However, in order to quantify the important soil element N, the nitrogen (N<sub>2</sub>) in the air must be excited at the same time as the laser hits the soil, making it very difficult to measure soil N through LIBS. Researchers have reduced the interference of N from the air through methods such as vacuum treatment and inert gas purging. Moreover, the main atomic emission peak of the P in soil lies in the ultraviolet range, which adds to the burden and complexity of the optical system.

LIBS offers the advantages of rapid and *in situ* soil measurement and is expected to enable on-the-go measurement similar to that on Mars rovers. However, the measurement of bioavailable nutrients has always been its biggest obstacle. As a typical atomic spectroscopy technique, LIBS can only detect nutrient elements in the soil, without distinguishing their molecular forms. This greatly limits its practical application in agriculture.

### 2.4. $\gamma$ -ray detection: mapping with isotopes

Some nutrient elements in the soil exist as isotopes, which maintain a certain proportional relationship with the total amount of the element. These isotopes continuously radiate cosmic rays. Based on this knowledge, an ingenious method has emerged that involves measuring isotopes with a  $\gamma$ -ray detector and then inferring the total amounts of elements in the soil based on the isotopic ratio. Since this method does not require contact with the soil nor any pretreatment, measurements can be carried out very quickly [13]. By installing  $\gamma$ -ray detectors on agricultural machinery, it is even possible to measure while moving, thereby generating real-time maps of nutrient element abundance for the studied plot of soil. A soil computed tomography (CT) scanning vehicle developed by SoilOptix (Canada) realizes fast and efficient soil nutrient mapping based on  $\gamma$ -ray spectroscopy. By passively absorbing four isotopes (<sup>137</sup>Cs, <sup>40</sup>K, <sup>238</sup>U, and <sup>232</sup>Th) naturally emitted by the soil, high-resolution digital soil mapping of multiple soil properties such as soil macro-elements, trace elements, and texture can be achieved [14]. This method relies on the stability of the isotopic ratios. Hence, it is often necessary to calibrate the nutrient elements in the area to be tested in advance and deduce the changes in the total amount of elements based on the measured changes in isotopes [15]. Since the calibration process requires laboratory analysis, this makes the measurement process quite complex. Moreover, if weather conditions (e.g., rainfall) or agricultural operations (e.g., fertilization) disrupt the isotopic ratios, the accuracy of this sensing method can be greatly affected. However, the aforementioned issues are inevitable in practice.

## 3. Conclusions

In summary, the sensing methods described herein vary in their measurement principles, and each has its own strengths and limitations in terms of measurement targets, methods, sensitivity, and convenience. These are just a few typical soil sensors that have been extensively studied. In fact, various sensors based on new principles are continuously emerging. In an important current trend, an increasing amount of research is applying artificial intelligence—especially deep learning algorithms—to soil sensors, constantly expanding the functions and performance of the sensors [16]. In one study, researchers developed a “disposable” low-cost soil NH<sub>4</sub><sup>+</sup>-N sensor that measured the generation of ammonia gas through chemical reactions; based on the NH<sub>4</sub><sup>+</sup>-N sensor, soil NO<sub>3</sub><sup>-</sup>-N content could also be obtained by training a neural network with other soil physicochemical indices such as compaction, pH value, and moisture content [17]. From the perspective of precision and smart agriculture, *in situ* sensors that do not require pretreatment and can even be directly buried in the soil for measurement are the ultimate goals of soil nutrient sensor development. From the perspective of soil science, although the current goals for nutrient measurement are diverse, including total N, P, K, trace elements, organic matter, and so forth, solving the onsite measurement of nutrients that plants can directly absorb (e.g., NO<sub>3</sub><sup>-</sup>-N) is the top priority for development.

### CRediT authorship contribution statement

**Daming Dong:** Writing – original draft, Conceptualization. **Ning Wang:** Writing – review & editing. **Hongwu Tian:** Writing – original draft. **Shixiang Ma:** Writing – original draft. **Chunjiang Zhao:** Conceptualization, Supervision, Investigation.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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