Optical Sensing Methods for Assessment of Soil Macro-nutrients and other Properties for Application in Precision Agriculture:: A review

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Abstract: ***With the advancement in science and technology, a lot of attention has been focused worldwide in the agricultural sector. With the ever increasing population, the demand for crop cultivation has raised enormously which in turn has lead to increased use of fertilizers to meet the demands. However, over application of fertilizers besides hampering the quality of crops, also leads to ecological imbalance by polluting water bodies as well as ground water due to chemical run off. So with the increasing awareness of fertilizers effects on environment and quality of soil as well as crops, issues like precision agriculture and site specific management has come to the forefront of present day technological development in agriculture and ecology. Nitrogen, phosphorous and potassium are three main macronutrients required for plant growth and are also the main constituents of fertilizer. So, researchers worldwide are trying to develop ways for on-the-go in-situ sensing and assessment of soil properties, so as to optimize the amount of fertilizers to be used while increasing the productivity without causing damage to the environment. In this review, efforts have been made to review the optical sensing technologies adopted by various researchers in last 15 years and thereafter identify the gaps and challenges and recommendations for required attention and work in this field.***

Keywords: Precision Agriculture, Nitrogen, Phosphorous, Potassium, Fertilizer, Near Infrared Reflectance Spectroscopy (NIRS), Raman Spectroscopy, Attenuated Total Reflectance Spectroscopy.

1. Introduction

Good Health is one of the prime concerns for every human being today. And to be healthy the quality of food is a big determinant. With the ever increasing population, the demand for food has also increased exponentially which in turn has led to the increased use of fertilizer to meet up the requirement. However, besides ecological concerns and the cost increased amount of fertilizers can cause serious health issue as well as effects the plant growth. This has gained attention of researchers worldwide to find effective ways to optimize plant yield while minimizing the application and consumption of fertilizers. The macronutrients Nitrogen (N), Phosphorous (P) and Potassium (K) commonly known as the NPK trio are the most important nutrients for plant growth and are also the main ingredients in any fertilizer. A lot of attention has been focused in this area in the recent years, particularly in the area of precision agriculture and site specific management procedures for obtaining localized on the go measurement of NPK in any soil.

NPK i.e., Nitrogen (N), Phosphorous (P) and Potassium (K), represent the three most important nutrients in agriculture and are the prime ingredients in almost all fertilizers.

- **Nitrogen:** it plays a fundamental role in the manufacture of chlorophyll in all plants and is an essential element of enzymatic proteins which catalyze and regulate the biological process responsible for plant growth. In this regard, nitrogen is one of three most essential macro nutrients.
- **Phosphorus:**It is another of the three macro nutrients required for plants for proper growth and in particular plays a significant role in root growth stimulation.
- **Potassium:** It plays a very important role in stomatal control in plants which effects water regulation and CO_2 exchange as well as enzymatic processes that enable photosynthesis. It is also essential in the manufacture and transport of sugar, starches and proteins, aiding in the development of straight leaves and quality fruit.

The use of fertilizer for increasing crop production dates back to 19th century, however controlling the rate of application of fertilizers in accordance with the type of soil or crops has been historically impractical and challenging until a couple of decades ago. Conventional laboratory chemical analyses techniques though gives good results but seems impractical when employed for precision fertilization [1]. There has been a significant development in sensing technologies for precision agriculture and site specific management methods in the last decade, to determine soil properties like pH, texture, salinity and organic matter, but routinely obtaining localized in-situ and on-the-go measurements of N, P and K still remains an open challenge.

Precision agriculture also called site specific crop management, is a soil and crop management system that assesses variability in soil properties and nutrient fields, to optimize inputs such as fertilizer and herbicides based on information obtained at site specific location.

Soil nutrient testing is a management tool that can help to estimate the amount of available nutrients in soil and thereafter guide the efficient use of fertilizers. Conventional soil testing methods are very time consuming, costly and also limit the number of samples that can be tested, making it difficult to characterize spatial or temporal variability in soil nutrient level within the field.

So, this review has been made with an objective to study about the sensing technologies and fundamental measurement principle in this field and discuss about the various issues, challenges and gap with the existing literature and hence find out the scope of future work in this field.

2.Sensing Technologies for Soil Quality Assessment

Broad reviews of various types of sensing techniques to measure the various nutrients present in soil have been presented in [1].

Most of the soil nutrient sensing techniques described in literature involve one of the two methods:

- ***Optical Sensing*** that uses reflectance spectroscopy to detect the level of energy absorbed/reflected by soil nutrients.
- ***Electrochemical Sensing*** that uses ion-selective electrodes which generate a voltage or current output in response to the activity of selected ions.

However this review focuses mainly on optical sensing methods and principles for measuring the macronutrients and other properties in soil.Optical sensing approaches are being investigated and studied by researchers worldwide due to their attractive advantages over electrochemical technology due to their non-destructive measurement nature and no need to take sample [2]. Measurement of reflectance, absorption or transmittance characteristics of a material provides a non-destructive and rapid technique to evaluate its properties. Determination of the amount of energy reflected from soil surface in a particular spectral range is the most popular approach in agriculture [3].Optical sensors are frequently affected by the different soil properties and exhibit different response in different regions of the spectral field which provide the opportunity to separate several effects with a single sensor response.

A chronological summary of optical sensing methods employed in past 15 years is presented below in table1:

TABLE 1:OPTICAL SENSING METHODS AND PARAMETERS DETECTED

Year/citation	Method	Parameters detected
[4] 1999	NIR spectroscopy	Nitrate content
[1]2001	NIR spectroscopy	OM, Soil moisture, CEC
[5] 2002	Admittance spectroscopy	Variation in nutrient content
[3] 2004	VIS-NIR sensor MIR spectroscopy	Soil organic carbon, Nitrate, moisture content.
[18] 2006	MIRS	Nitrate
[6] 2006	UV, VIS,NIR absorbance spectroscopy	phosphorous
[7] 2007	VIS-NIR sensor	C, MC, pH and P
[17] 2007(**patent**)	Raman Spectroscopy	Phosphorous
[2] 2009	Optical diffuse sensing in visible and NIR and MIR ranges UV-Vis-NIR spectroscopy	Nitrogen Phoshorous
[8] 2010	• Near-infrared-diffuse Reflectance Spectra • ATR spectroscopy • MDRS • Raman Scattering • Reflectance spectroscopy	Nitrate Phosphorous
[9] 2011	Optical Fibre Sensor (UV source)	Ammonia
2013 [10]	NIR absorption (MEMS based)	Nitrogen
2015 [11]	Diffuse reflectance spectroscopy	Total Nitrogen and Organic Matter
2015 [12]	Diffuse Reflectance Spectroscopy	Soil pH, moisture content however poor results for total phosphorous and potassium.

3.Spectroscopic Methods for Sensing Soil Properties

Advances in spectroscopy have provided new methods to determine concentration of elements in industry. The commonly employed methods are Ultra Violet, Visible and Infrared reflectance spectroscopy. It has advantages in determining soil properties rapidly and non-destructively.

3.1. Near Infrared spectroscopy

NIRS involves measurement of photons diffusely reflected by a sample interrogated with a polychromatic source of optical radiation in the infrared range. The basic principle underlying NIRS analysis is the theory of simple harmonic oscillator. Any two atoms sharing a bond can be considered as a simple harmonic oscillator system that has resonant characteristics which are dependent on the two constituent masses in the bond and the “spring” constant describing the force between them. The given sample is irradiated with frequencies similar to vibrational frequencies of the bonds in the sample will be absorbed while others will be reflected back. The diffuse reflectance spectra from the sample are recorded with a spectrophotometer to form a reflectance spectrum which indicates the intensity of light collected as function of wavelength. Regions or wavelength where the intensity is less indicates the regions of absorption and indicates the presence of the molecular bonds present in the sample. Overall NIRS has been referred to as one of the most amenable method for on-the-go site specific soil assessment [1].

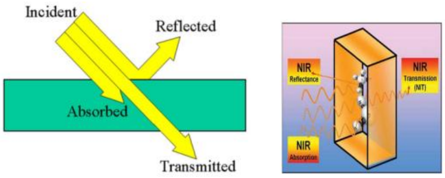

Figure1: **Near Infrared Reflectance**

NIRS is one of the most common methods employed in optical sensing of Nitrogen content in soil. Recently in [11], a portable instrument based on *Near Infrared Diffuse Reflectance Spectroscopy* has been developed to predict the constituents of total nitrogen and organic matter in soil. They demonstrated that absorption peaks for this constituents existed around 850nm and 940 nm. In a study [12], the authors have demonstrated that optical reflectance spectroscopy in VIS-NIR is an ideal tool for estimation of soil nitrogen, pH, and OM content. In [6], the absorbance spectra of soil was studied by employing UV-VIS-NIR spectroscopy for sensing the concentration of phosphorous in soil. In [7], a VIS-NIR sensor has been developed for measurement of carbon, moisture content, pH and phosphorous. Here a mobile fiber type VIS-NIR spectrophotometer (306.5nm-1710.9) was used to measure the soil spectra in the reflectance mode. And the results obtained showed the best correlation for Moisture content.

In [13] NPK sensing has been achieved by developing a fiber optic sensor based on colorimetric principle where absorption of light by a solution results in variation in the output of the sensor. In [14], a NIR soil sensor has been developed for soil moisture and organic matter detection. In [10], A near infrared absorption spectrometer using MEMS near infrared light source had been assembled to predict the total nitrogen content. In another work [19], an LED based optical sensor for analysis of soil nutrients has been developed for detection of ammonia nitrogen, Nitrate nitrogen, available phosphorous, available iron, exchangeable manganese and exchangeable calcium. The detection was done based on the color changes caused by addition of addition of certain chemical reagents.

3.2. Attenuated Total Reflectance Spectroscopy (ATRS)

Basically ATR is same as NIRS, however here instead of irradiating the sample with a spectrum of infrared radiation and collecting the diffuse reflectance spectra, here the infrared energy is directed into the crystal which is placed in direct contact with the sample of interest and has higher refractive index than the sample. The incident energy is reflected several times within the crystal creating an evanescent field at the interface between the crystal and the sample. As the internally reflected energy finally exits the system, it is directed towards the spectrophotometer to produce the reflected spectrum for the sample. ATRS utilizes the principle of Total Internal Reflection. The beam entering the crystal will undergo several internal reflections, when the angle of incidence at the interface between the sample and crystal is greater than the critical angle. The beam penetrates a fraction of wavelength beyond the reflecting surface and when a material that selectively absorbs radiation, such as soil is in close contact with the reflecting surface , the beam losses energy at the at the wavelength where the material absorbs. The resultant attenuated radiation is measured and plotted as a function of wavelength by the spectrophotometer and give rise to the absorption spectral characteristics [15]. The crystal used in ATR is made of Zinc Selenide, germanium, and thallium iodide.

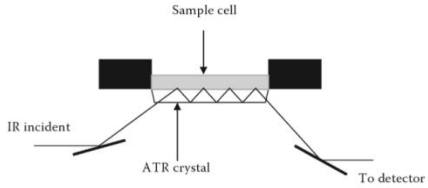

Figure 2: Schematic of a typical Attenuated Total Reflectance (ATR) cell.

ATRS provides a very good estimation of Nitrogen, soil moisture content and organic content in soil but as the instrumentation required is expensive and delicate, it is not suitable for in-situ measurements [1]. Attempts were made in [4] to employ mid-infrared reflectance for soil nitrate determination. Soil pastes from ten different soils, including sandy loam, clay, and peat soils, were analyzed for soil nitrate contents using the Fourier transform infrared (FTIR) attenuated total reflectance (ATR) technique. Direct determination by ATR spectroscopy requires minimal sample preparation, but advanced data processing is necessary to minimize interferences due to water and soil constituents. Also dry soils were very challenging to interrogate using this method. Linker et al in [18, 20-23] used Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectroscopy in the mid-infrared range to measure nitrate content in soil solutions and pastes. Here MIRS was employed to detect the presence of nitrate in various types of soil. A spectrophotometer with ATR crystals was used for the measurements of soil pastes. Wavelet analysis was then applied to soil spectra collected and calibrations equations were developed, resulting in values for coefficient of determination of R^2 as 0.99.

3.3. Raman Spectroscopy

Raman Spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and are reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the **RAMAN Effect**.This shift in the frequency provides information about the sample under study.The spectrum of the observed scattered frequencies is again indicative of the molecular composition of the sample under study. In Raman scattering the Raman shifts are independent of the excitation wavelength since they are a function of the investigated constituent and not the wavelength of the incident energy. Although Raman Spectroscopy is an established technique, it has been seldom used to detect phosphorous in soil [1].

In [6], the authors have explored the use of Raman Spectroscopy for phosphorous analysis in soils and developed a portable operating unit at 785nm. Raman Spectroscopy Raman Spectroscopy provides good result for phosphate detection, besides the instruments used are relatively low cost and can be employed for in-situ sensing. Raman spectra signature can provide structural information based on vibrational transitions of irradiated molecules. In

[16], the soil phosphorus concentration was studied based on Raman spectroscopy. 15 sand soil samples with different phosphate content were made in laboratory and the Raman signatures were measured. The relationship between sand soil Phosphorus concentration and soil Raman spectra was explored. Calibration results showed good accuracy and thus demonstrated the potential of Raman spectroscopy in phosphorous detection. In 2007, Lee and Bogrekci invented (patented to their name) [17], an apparatus and method for detecting phosphorous in soil and vegetation. The portable RAMAN based sensor had the capability to measure phosphorous concentration both in wet and dry soils. The sensor in the invention uses a laser source at 785nm.A method for detecting nutrients in soil phosphorus, nitrogen, potassium, potash, magnesium, sulfur, and other trace vitamins, minerals, and elements) is also part of the present invention, wherein a sample of soil is placed into a sample compartment. In one embodiment, the sample compartment includes a means for drying, grinding, and/or sieving the soil sample. The soil sample is then analyzed using a laser beam, where the laser beam is reflected and collected through a Raman probe and fiber-optic cable by a spectrometer. In one embodiment, the spectrometer measures the Raman spectrum in a Wave number range of about 350 to 3640 cm. The data generated by the spectrometer is then communicated to a processor to calculate the phosphorus concentration, in the soil sample.

4.Discussions

Although a lot of work is being done in the area of precision agriculture, in-situ sensing of macronutrients in soil still remains an open challenge. Conventional soil testing methods in laboratory are expensive, labor intensive and time consuming. Studies show that optical sensing approaches particularly NIRS have the potential to sense the nitrogen and organic matter in soil, but typical spectrophotometers still has the disadvantage of high cost and bulkiness. This makes them unsuitable for in-situ measurements.

- Though VIS- NIRS spectroscopy has been found to be a reliable tool for the prediction of soil nitrogen content, but it showed poor results for the prediction of P and K, since P and K could not form absorbers in NIR region.
- Direct determination by ATR spectroscopy requires minimal sample preparation, but advanced data processing is necessary to minimize interferences due to water and soil constituents. Also dry soils are very challenging to interrogate using this method.
- Raman spectroscopy and UV photoluminescence has the potential for measuring soil phosphorous contents, however as compared to Nitrogen, very less attention has been given in this area mainly because of the cost involved.

Reflectance spectroscopy for analysis of potassium in soil is a challenging task as direct correlation of reflectance observations with potassium content tends to be weaker than that observed for Nitrogen or Phosphorous.

5.Conclusion

Various optical sensing approaches has been reviewed and it has been found that, overall these sensing techniques have the potential to detect the presence of soil macro-nutrients, however in-situ measurements of nutrients still remains an open challenge due to factors such as expensive and bulky spectrophotometers. Also, in the previous section, various challenges and gaps in literature have been identified. Though considerable progress have been made in this area in last decade, but still fully integrated NPK detection system remains a challenge. So, it is clear that there is an ardent need for an in-situ multi-target optical sensor system.

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