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Printed Nitrate Sensors for In-Soil Measurements

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Abstract

Managing nitrate is a central concern for precision agriculture, from delineating management zones, to optimizing nitrogen use efficiency through in-season applications, to minimizing leaching and greenhouse gas emissions. However, measurement methods for in-soil nitrate are limited. State-of-the-art soil nitrate analysis requires taking soil or liquid samples to laboratories for chemical or spectrographic analysis. These methods are accurate, but costly, labor intensive, and cover limited geographic scope. Some colorimetric tests are available which give qualitative nitrogen information. Other researchers rely on measurements of applied nitrate, leaching, and uptake to calculate mass balance equations for larger areas, but errors in estimates of inputs or outflows lead to errors in nitrate concentration. Alternatively, NDVI or other vegetative indices can be used to estimate spatial variation of nitrate in plant material, but by the time nutrient deficiencies are evident in these indices, it may be too late to correct.

Quantitative soil nitrate sensors at high spatial resolution and multiple depths are needed to fully leverage precision agriculture technologies. Printed potentiometric ion-selective nitrate sensors could fill this need because they are small, low power, involve no moving parts, and are mass-producible. We have fabricated printed nitrate sensors and characterized them in aqueous solutions and in soil media. We have made sensors using two families of materials: degradable and non-degradable. Non-degradable sensors are made from plastics, acrylics, and metals, and are designed to be robust for repeated insertion into soil, and have a long lifetime. Degradable sensors are made primarily from wood, paper, waxes, water-soluble plastics, and conductive carbon, and would be suitable for deployment at high spatial density in fields where electronic waste buildup is undesirable.

Both degradable and non-degradable sensors show sensitivity to nitrate near the theoretical limit governed by the Nernst equation, and are not significantly impacted by the presence of sulphate, chloride, phosphate, nitrite, ammonium, potassium and magnesium, but showed that high concentrations of calcium can be problematic. The sensors were characterized and calibrated in real soils of varying textures and water contents.

Keywords.

Nitrate sensor; proximal soil sensor; printed electronics; sensor-based nutrient management

Introduction

Precision Agriculture aims to use resources efficiently by applying only as much water and fertilizer as is needed at the precise location and time. This approach relies on data, which comes from sensors. While optical remote sensing, such as NDVI indices, can be used to monitor plant health, and yield monitors on GPS-enabled harvesters can provide end-of-season spatial variation information, measuring nitrate in the soil at high spatial resolution and in real time remains a challenge. State-of-the-art nitrate measurements in both soil and water quality monitoring involve taking samples from the environment or field to a laboratory, where they can be analyzed with chromatography or spectrographic methods (Sempere 1993). Low cost proximal soil nitrate sensors connected in a wireless network could increase the impact of other precision agriculture technologies by providing real-time, high spatial resolution data of nitrate in soil.

Potentiometric sensors are a promising class of sensors for in-soil nitrate monitoring because they involve no moving parts, require only simple read-out electronics, and can be mass produced. A potentiometric sensor is made of two electrodes: an ion-selective electrode and a reference electrode. The ion-selective electrode is a conductor which is coated with an ion-selective membrane. This membrane contains an ionophore—a specially designed chemical which binds selectively and reversibly to the ion of interest (Moody 1970, Armstrong 1990, Buhlmann 2012). As the concentration of nitrate in the vicinity of the ion selective electrode increases, the electric potential on that electrode becomes more negative. Reference electrodes are made of silver/silver-chloride, which maintains a stable potential as ion concentrations in the environment change (Gilbert 1947).

The principle figure of merit for a potentiometric ion-selective sensor is its sensitivity. Based on the Nernst equation, the sensor will have a linear change in potential for a logarithmic change in nitrate concentration, thus sensitivity is measured in (mV/decade), where one decade is a factor of 10 change in nitrate concentration. This logarithmic behavior holds whether concentrations are measured in mM, ppm, or $\mu\text{g/g}$ dry soil. At room temperature, an ideal sensor will have a sensitivity of -59 mV/decade, with higher nitrate concentrations corresponding to lower voltages because nitrate carries a -1 charge. The selectivity of a sensor is another important figure of merit; a nitrate sensor should respond only to nitrate, but real sensors can be impacted by other ions.

The aims of this study were to characterize the impact of various chemicals found in soil, the impact of soil texture, and the impact of soil water content on the performance of printed potentiometric nitrate sensors. This data will be used to calibrate sensors deployed in early-stage field trials, and inform the development of future generations of sensors.

Materials and Methods**Sensor Fabrication**

The sensors were made using low-temperature, solution-processing techniques, which can enable large-scale fabrication. The ion-selective electrodes were made by screen-printing a conductive carbon ink (Creative Materials 114-34A - Solvent-Resistant 150 Ohm/Square Carbon Ink) on a 100 μm thick Polyethylene terephthalate (PET) substrate. The electrode was a 3.5 mm diameter circle, connected to a 1 mm wide conductive line. The electrode was encapsulated by a layer of Teflon tape, with a pre-cut hole to expose the circular part of the electrode. The ionophore membrane, which contains a nitrate-selective ionophore and PVC dissolved in a solvent, was drop-cast over the circular part of the electrode. As the solvent evaporated, the membrane formed.

The reference electrodes were made by screen-printing a silver/silver-chloride ink (Engineered Materials Systems, Inc. CI-4001) on a 100 μm thick PET substrate. The reference electrodes had

the same geometry, and the same Teflon encapsulation as the ion-selective electrode. A layer of carbon nanotubes was drop-cast on the reference electrode, followed by a solution of NaCl, NaNO₃, and poly(vinyl butyral).

Both electrodes were glued to an acrylic stake for mechanical support. Wires were attached using 8331D silver conductive epoxy (MG Chemicals), and the joints protected with a layer of Gorilla Epoxy. The sensors were connected to circuit boards which used a custom pre-amplifier circuit to measure the difference in voltage between the two electrodes with very low current draw. This voltage was read by an Arduino board (MKR WiFi 1010) and reported every 1 minute using WiFi.

Sensitivity and Selectivity in Solutions

To measure sensitivity to nitrate in aqueous solutions, a set of beakers were prepared with known concentrations of NaNO₃ between 0.01 mM and 100 mM. Each sensor was placed in one beaker, left for 3 minutes to stabilize, and the potential difference between the electrodes was recorded. The sensor was then moved to the next beaker with a different NaNO₃ concentration, and the process repeated.

To measure selectivity, a similar set of beakers were prepared. Each beaker contained 1 mM NaNO₃ as well as an interfering ion, at the concentrations expected to be found in soil. The difference between the baseline potential measured in 1 mM NaNO₃ and the potential measured in the beaker which also contains the interfering ion can be attributed to that ion.

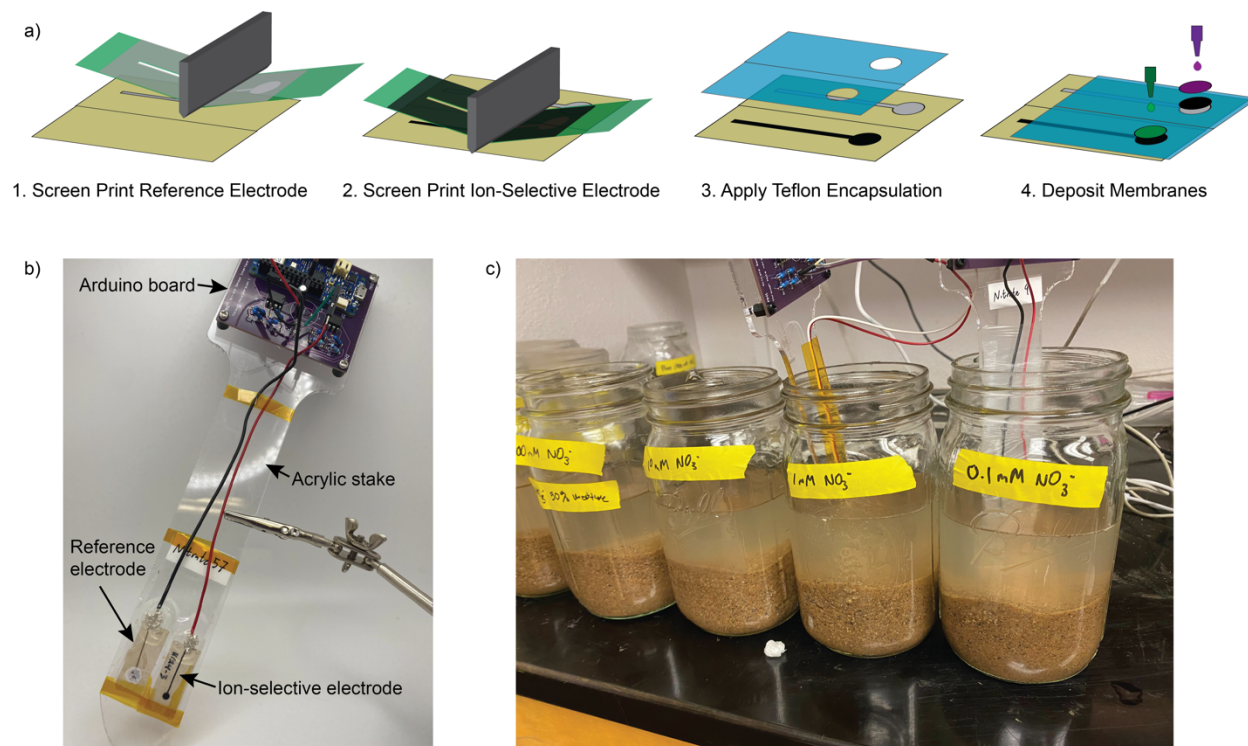


Fig 1. a) The fabrication process for the sensors involved screen printing the electrodes, encapsulating them with Teflon tape, and depositing membranes. **b)** The sensors were mounted on acrylic stakes for ease of handling in soil. They were connected to wifi-enabled Arduino boards to report sensor measurements. **c)** Measurement set up to measure sensitivity to nitrate in saturated sand.

Characterization in Soil

To measure the sensitivity of nitrate sensors in soil, sets of six jars were prepared. One set of jars was filled with sand, another with a Rindge series soil high in peat, and a third set with a high-clay content soil. The jars were watered with 0, 0.1, 1, 10, 100, and 1000 mM KNO₃ solutions. Each sensor was inserted in one container and left for at least three minutes until the potential reading stabilized. After measurement in one container, the sensor was removed, rinsed with deionized water and inserted into the next container. After the sensor measurements were completed,

samples from each jar of soil were taken and KCl extractions were run to determine total nitrates present in the soil, including nitrate present before watering.

To measure the impact of soil moisture, another set of six containers were prepared of each soil type. All containers were watered with 10 mM nitrate solution to varying moisture levels ranging from saturation to completely dry. Again, sensors were moved from container to container, and the potential was recorded in each container.

Results

The average sensitivity of sensors in aqueous solution was -44 mV/decade. In saturated sand, the average sensitivity was -43 mV/decade, which indicates that good functionality possible in porous media. Sensitivity in peat soil was somewhat lower, while sensors in clay soil had the lowest sensitivity.

In interference studies, sulphate, chloride, phosphate, nitrite, ammonium, potassium and magnesium, were found to have small interference coefficients, but calcium is a significant source of error in measurements.

Accurate measurements require a continuous liquid path between the two electrodes, so measurements are not possible in very dry soil. In sand, moisture levels above 20% are sufficient for reliable measurement, while peat soil requires at least 30%. Measurements made below the moisture threshold appear as extremely low nitrate concentrations.

Conclusion

Potentiometric nitrate sensors are a promising tool to measure soil nitrate in the field at large scale because they are simple to fabricate, involve no moving parts, and only basic low-power electronics to take a measurement. Printed potentiometric nitrate sensors show good sensitivity and selectivity in aqueous solutions and sand, but field soils are more complex. Work remains to calibrate sensors for use in real soils, to understand the soil types and conditions where reliable measurements can be made, and to improve the sensors so they function in a wider range of real soil conditions.

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