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Field Sampling and Electrochemical Detection of Nitrate in Agricultural Soils

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Abstract. Nitrate is an essential plant nutrient and is added to farm fields to increase crop yields. While the addition of nitrate is important for production, over-fertilization with nitrate can lead to leaching and contamination of water bodies. Increased nitrate loading in water sources then leads to eutrophication and hypoxia in downstream regions. Many efforts are being made to accurately control nitrate fertilizer additions to fields. Here, we present a soil sampling device that directly samples soil nitrate. First, water is injected into soil, collected and filtered through a porous ceramic filter via vacuum/suction. Next, this filtered sample is analyzed for nitrate using an electrochemical sensor with disposable electrodes also developed in this work. Specifically, these disposable sensors utilize paper electrodes functionalized with gold nanoparticles. Gold acts as a catalyst for the reduction of nitrate to nitrite. This reduction is then detected using electrochemical methods with a limit of detection of 8.6 µM. This direct sample collection and analysis system provides rapid, accurate detection of nitrate without the need for laborious soil sample collection and shipment for subsequent laboratory analysis. This system can aid both farmers and researchers as they monitor nitrate levels in soil over the course of a growing season and reduce the impact of agricultural leaching and drainage losses on water quality.

Keywords. *nitrate, gold nanoparticles, disposable electrodes, electrochemical sensor*

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Introduction

Fertilizer additions in agriculture are of vital importance as agricultural professionals seek to maximize yields and minimize impacts to the landscape. These fertilizers are comprised primarily of nitrate and ammonium and are widely broadcast onto fields, particularly in the Midwestern United States. Over application of these chemicals, however, can lead to water quality issues like eutrophication and hypoxic zones in the ocean. A growing number of research groups have dedicated themselves to tackling this large problem at multiple levels of the agricultural system through precision application, modeling, and rapid field testing of applied chemicals. One major area of development in this field is sensors. Sensing plays a major role in precision agriculture systems as chemical additions to agricultural fields must be monitored both for efficiency (plant uptake in the case of fertilizers) and environmental fate and transport of these chemicals. In this we work we describe the development of an agriculture sampling system for field testing of nitrate. This system is comprised of a soil water collection system and a novel electrochemical sensing chip.

Results

Soil sampler specifications

The functional probe developed in this work (shown below in **Figure 1**) is an adapted form of a conventional soil probe whereby the probe is inserted into soil to isolate a small representative column (A. Abbas & J. Brockgreitens, "Soil Sampling and Sensing Device", *IP Disclosure case # ROI 20160039 (July, 2015)*). Upon insertion into soil, this probe introduces water from the top of the probe and recovers the water through filtered porous openings located along the side of the probe via suction/vacuum pump. This filtered water is then introduced to the portable sensor chip system. After analysis the probe can be removed from the soil and rotated to eject the captured soil core.

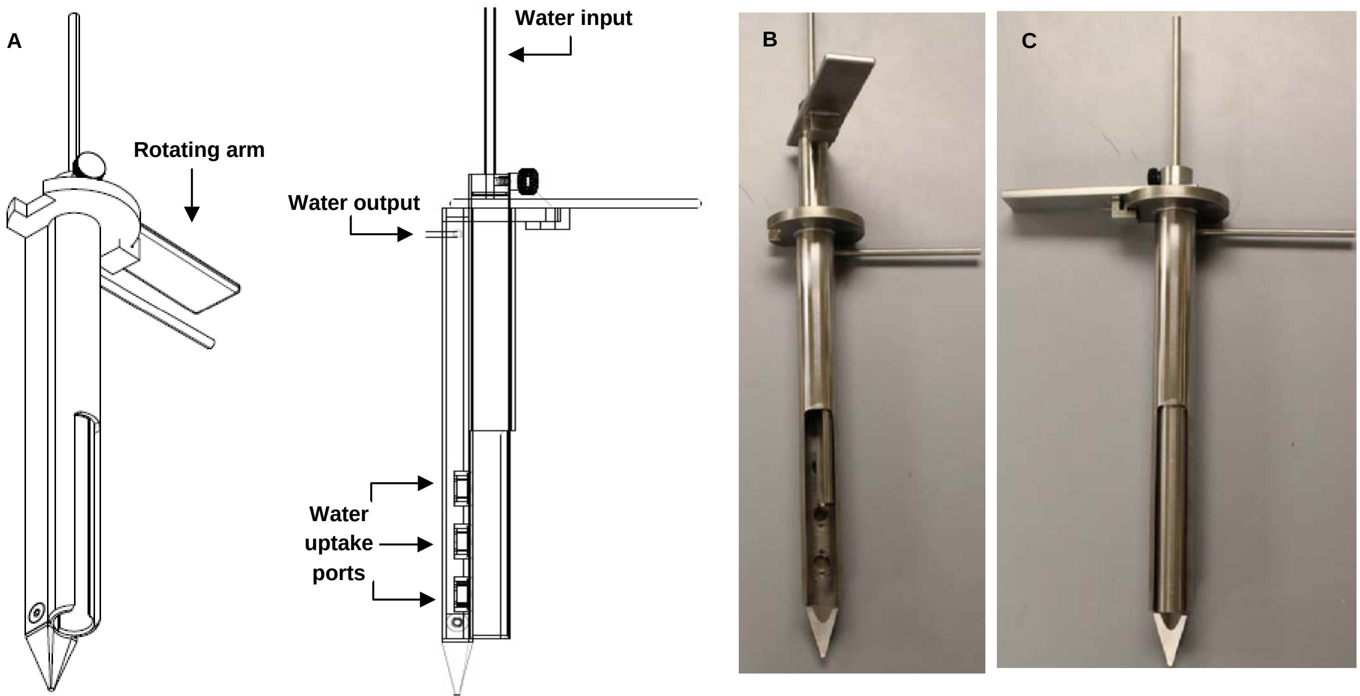

Figure 1: Schematic of the soil water recovery device with pertinent pieces labeled (**a**). Photographs of the device fabricated using stainless steel in both the open rotated position (**b**) and the closed rotated position (**c**).

Soil water capture

This probe can be easily inserted into soil like a conventional soil probe. Once inserted, water can then be added into the top of the probe. This water is this collected via suction through ports on the side of the probe. This water is then taken up through a sealed chamber and out to a container where the water sample can be quickly analyzed with the sensor chip and subsequently ejected. **Figure 2** shows the pathway of water through the device.

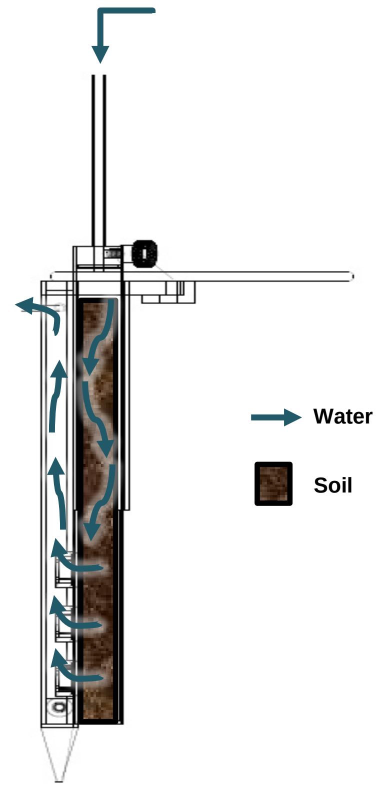

Figure 2: Schematic of water flow through the fabricated device.

Electrochemical detection system

After recovery the collected soil water is then filtered and analyzed using a sensor chip fabricated from gold and selenium nanoparticles (Bui et al, 2016). Briefly, gold nanoparticles were deposited onto print carbon electrodes. These particles catalyze the reduction of nitrate in solution. This reduction is then then yields a change in current that can be tracked electrochemically. These sensor chips, while disposable, are effective for up to 20 consecutive measurements and have a limit of the detection of 8.6 µM. **Figure 3** shows the final measurement of nitrate in solution (Bui et al, 2016).

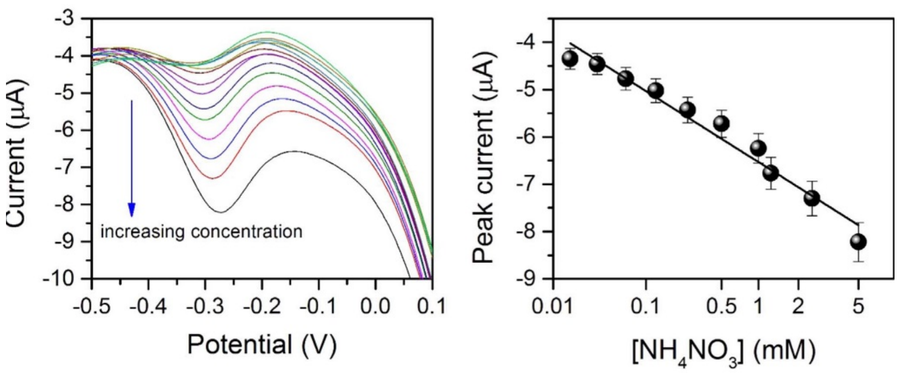

Figure 3: Nitrate measurements as analyzed by the gold nanoparticle/selenium nanoparticle sensor chips.

Conclusion

In this brief report, we describe current research concerning soil sampling. In this work, a soil water collection system has been developed that can successfully recover soil water. While this work is still ongoing, the combination of rapid sensor chip technology with a novel soil water recovery system has a great deal of potential in application for precision agriculture. Future work in this project includes fully deploying this system in field scenarios and creating an automated sampling system that can be implemented in a farming vehicle.

References

Bui, M. P. N., Brockgreitens, J., Ahmed, S., & Abbas, A. (2016). Dual detection of nitrate and mercury in water using disposable electrochemical sensors. *Biosensors and Bioelectronics*, *85*, 280-286.