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Ion-Selective Electrode Offers Accurate, Inexpensive Method for Analyzing Soil Solution Nitrate in Remote Regions

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Nitrogen (N) applied as fertilizer is subject to runoff and leaching. Nitrate (NO_3^--N) concentrations in soil solution reflect the impacts of farm management on N cycling. Some of the most remote regions in the world are undergoing rapid land-use change, yet there are major barriers to conducting research in these locations. Fortunately, new tools such as ion-selective electrodes (ISEs) provide low-cost and simple methods for conducting chemical analysis in the field. Researchers compared soil solution NO_3^--N concentrations measured using an ISE with concentrations measured on a colorimeter (cadmium reduction) and found good agreement ($r^2 = 0.96$, $P < 0.0001$) between the two methods. The ISE is also 66 times less expensive than in-country laboratory analysis or shipping and analyzing the samples in the United States. Thus, the ISE is an excellent tool for rapid analysis of N in soil solution, providing critical information on N dynamics in remote regions.

Keywords Field methods, ion-selective electrode, leaching, nitrate

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Introduction

Nitrogen (N) is essential to plant growth and is often limiting in agricultural systems. Humans have doubled the terrestrial nitrogen (N) supply through the addition of fertilizers (Carpenter et al. 1998; Galloway et al. 2008), vastly improving crop yields around the world. However, fertilizer use has resulted in unintended off-site N losses through agricultural runoff, leaching, and trace gas emissions (Ladha et al. 2005; Robertson and Vitousek 2009). Unlike most regions, nearly 80% of countries in sub-Saharan Africa (SSA) face problems of N scarcity (Liu et al. 2010). The Alliance for a Green Revolution in Africa (AGRA) has called for a sixfold increase in N fertilizer application in the region by 2015 (from 7 to 50 kg ha^{-1}; IFDC 2006) to improve crop yields and increase food security. However, it is unclear what the environmental consequences of such a huge shift in land-management practices will be given a long history of soil degradation and variability in soil type.

Currently, estimates of N loss from SSA agriculture have been estimated with inappropriate data from other tropical regions where soil types, climate, and land management

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are entirely different from those in SSA (Hickman et al. 2011; Færge and Magid 2004). There are major logistical barriers to measuring contamination in remote regions because of the lack of infrastructure and technical expertise. However, in recent years low-cost, field-ready environmental sensors, such ion-selective electrodes (ISEs), have been developed for more than 50 analytes, including nitrate N (NO_3^--N; Bakker and Pretsch 2002). Fertilizer application can increase NO_3^--N fluxes from agricultural fields through the downward movement of water through the soil column (leaching). There are several methods available for capturing infiltrating water (soil solution) using lysimetry. Past studies have shown the accuracy of ISEs to measure NO_3^--N in petiole sap (Hartz et al. 1993; Vitosh and Silva 1994), soil slurries (Adsett 1990; Thottan et al. 1994; Sibley, Adsett, and Struik 2008), and leaf tissue (Ott-Borrelli, Koenig, and Miles 2009). It appears that only one study has used ISEs to measure NO_3^--N in soil solution, and the concentrations were two orders of magnitude lower than concentrations measured in this study (Hartz et al. 1993). In this study, we validate their use for measuring NO_3^--N concentrations in soil solution leaching from agricultural fields. For research in remote parts of Africa, the laboratory is usually outside the country, or even continent, requiring costly and time-consuming shipping. In addition, NO_3^--N is a highly labile N species and subject to rapid transformations by microbial immobilization and denitrification, especially in nutrient-rich complexes such as soil solution. Thus, extended sample handling and transport times can introduce considerable measurement errors (Jenkins 1967; Degobbis 1973; Klingaman and Nelson 1976). The purpose of this work is to compare the accuracy of a nitrate ISE against standard chemical analysis to determine its utility in a remote setting where infrastructure for sample preservation, transportation, and traditional analysis is limited.

Materials and Methods

Study Sites

This study was conducted at two sites differing in climate (Table 1) and soil mineralogy: (1) Yala in the western Kenyan highlands with clayey soils of oxidic mineralogy and (2) Tumbi in midwestern Tanzania with sandy-loam soils of mixed mineralogy. Maize fields were established in a randomized complete block design (RCBD) on lands owned by

Table 1
Site characteristics and baseline household characteristics before MVP interventions (Palm et al. 2010; Nziguheba et al. 2010)

Site	Major soil type	Clay content (%) 0–20 cm[a]	Mean annual rainfall (mm)	Length of major rainy season	Mean annual temperature (°C)
Mbola, Tanzania	Alfisols	20.4 (12.1–35.0)	Unimodal 928	Nov–Apr	23
Sauri, Kenya	Oxisols	30.9 (17.3–45.9)	Bimodal[b] 1816	Mar–June	24

[a]Mean, range reported in parentheses.
[b]40 to 50% of the rain falls during the long rainy season, similar to the amount of rainfall during the one cropping season in Mbola.

the Kenya Broadcasting Center Nyamninia in Yala, Kenya, and at the Tumbi Agricultural Research Institute in Tabora, Tanzania. Yala, Kenya, receives 1816 mm of precipitation per year in two rainy seasons; the "long rains" extend from March through June and the "short rains" extend from October to early December. Tumbi, Tanzania, has one rainy season (from November through April) and receives 928 mm of precipitation on average during this period (Table 1). The mean annual temperature is similar in both sites: around 23.5 °C (Palm et al. 2010; Nziguheba et al. 2010).

Experimental Design

The RCBD experiments were established to determine the response of soil N dynamics to increasing levels of fertilizer N. Plots were amended with six different levels of inorganic fertilizer: 0, 50, 75, 100, 150, and 200 kg N ha^{-1}. In Tanzania, a seventh treatment of *Gliricidia* prunings at approximately 75 kg N ha^{-1} was added. Each treatment has four replicates, for a total of 24 plots in Kenya and 28 plots in Tanzania. Tension lysimeters were installed to collect soil water soil solution in plots receiving 0, 50, 75, and 200 kg N ha^{-1} (and the *Gliricidia* plots in Tanzania). Maize (*Zea mays;* Dekalb 8053) was planted in both locations at 30 × 75 cm spacing. Plots were 3 × 6 m, with a total of 80 plants per plot. Because of the rainfall patterns and soil texture, maize lines were ridged in Tanzania but not in Kenya. Lysimeters were installed at random within the center of the plots; plants in the outer two rows and lines were considered "buffer plants." Fertilizer was applied basally in a split application: one third at planting (using diammonium phosphate) and the remaining two thirds at topdressing (as urea).

In the clayey soils of Yala, Kenya, three lysimeters were installed in each plot at 15, 120, and 200 cm and in the sandy soils of Tumbi, Tanzania, they were installed at 50, 120, and 200 cm below the soil surface. Sands had much lower soil moisture content (5–10%) than the clays (30%) and therefore lysimeters had to be installed at a deeper to ensure good contact with soils. Tension lysimeters were constructed by attaching ceramic cups (SoilMoisture Corp., Goleta, Calif.) to a 1.25-inch diameter polyvinyl chloride pipe tube sealed at the end with a rubber stopper. Lysimeters were installed and allowed to equilibrate for 2 months prior to sampling. The day before sampling, lysimeters were purged of any water and an internal pressure of –0.05 to –0.06 MPa was applied. Solution samples were collected once prior to maize planting, daily for 3–5 days following planting, and weekly until top-dressing. Soil solution samples were collected daily for 3–5 days following top-dressing, weekly for 4 weeks after top-dressing, and biweekly until harvest.

Soil Solution Analysis

Soil solution samples were kept in acid-washed high-density polyethylene bottles to which a pinch of Thymol (5-methyl-2-[1-methylethl]phenol; Acros Organics; Thermo Fisher Scientific Inc., Waltham, Mass., USA) was added to inhibit biological activity. Within 3 days of collection, unfiltered water samples were analyzed for NO_3^--N using an ISE (Horiba, Inc. B-342; Kyoto, Japan) in country. The ISE has a two-point calibration (6.8 and 68 mg NO_3^--N L^{-1}), and was calibrated every 10 samples. Soil solution samples were analyzed for NO_3^--N on the ISE in triplicate and averaged (average standard error of the mean three analyses = 0.24 NO_3^--N L^{-1}). The electrode was triple-rinsed between samples with deionized water; however, the ISE rarely read zero with a blank. Instead, blank readings were typically less than 2 mg NO_3^--N L^{-1}, which is well below the detection limit for the instrument.

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When possible, samples were kept refrigerated, but due to frequent power outages, samples often remained at room temperature for extended periods of time. Soil solution was filtered through a Whatman filter (no. 42; 2.5 μm; GE Healthcare, Little Chalfont, UK) to remove any debris, and subsamples ($n = 161$) were transported to the Marine Biological Laboratory at Woods Hole, Mass. Inorganic NO_3^--N in soil solution was analyzed on a LACHAT QuikChem (LACHAT Instruments, Loveland, Col.) using cadmium reduction. All samples were diluted 1:10 (sample to deionized water) initially. Some concentrations exceeded the greatest calibration standard that was within the detectible range of the colorimeter and were diluted until detectible. A univariate regression was used to compare the NO_3^--N concentrations measured by the ISE and the colorimeter. The equation, r^2, and P value from that regression are reported (SAS Institute, Cary, N.C.).

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Results and Discussion

Univariate regression found a very strong, positive relationship between nitrate concentrations measured using the field method (ISE) and the standard laboratory method (cadmium-reduction colorimetry; $r^2 = 0.96$ and $P < 0.0001$; Figure 1). The concentrations of NO_3^--N in water samples ranged from 1 to 167 mg L^{-1}. Although the ISE's calibration range is 6.8 to 68 mg NO_3^--N L^{-1}, it still predicted concentrations with a reasonable degree of accuracy. Considering that error was introduced through dilutions for the colorimeter, the two methods agree quite well. Soil solution samples were filtered before running on the colorimeter to avoid clogging the system; however, we did not detect a difference in the methods that could be attributed to filtering or suspended particulates. This is likely because that soil solution was extracted using a porous cup and samples were essentially prefiltered. However, in a study of several soil slurries, the ISE reported similar concentrations in clear and muddy solutions, indicating insensitivity to suspended particulates (Figure 2). Thus, water samples collected from sources with greater suspended particulates (such as stream or well water) can also be analyzed for NO_3^--N on the ISE without filtering (saving both time and money). Finally, the per sample cost for NO_3^--N

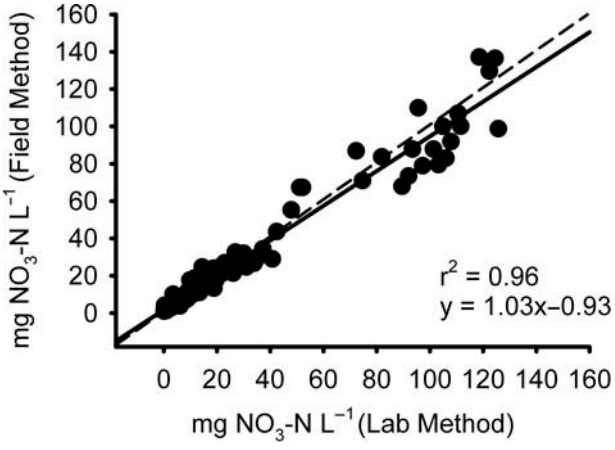

Figure 1. Comparison of nitrate concentrations in the soil solution measured using the laboratory method (colorimeter) and field method (ion selective electrode; $n = 161$). Solid line is the line of best fit, and dashed line is the 1:1 line.

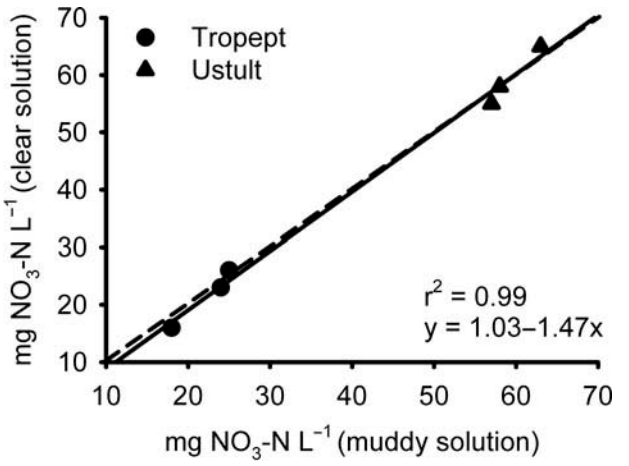

Figure 2. Comparison of nitrate concentrations in a clear and muddy soil slurries measured using the ion selective electrode. Solid line is the line of best fit, and dashed line is the 1:1 line.

Table 2
Cost analysis of running water samples for NO_3^--N using standard EPA methods (in-country and in the USA) compared to the ISE method

Method	Price ($USD)
Colorimetric	
Commercial laboratory NO_3^--N analysis in Nairobi	**$39.00 (per sample)**
Ship samples to USA on dry ice	$16.32 (per sample)
Commercial laboratory NO_3^--N analysis in USA	$21.13[a] (per sample)
Total shipping and NO_3^--N analysis	**$37.45 (per sample)**
ISE	
Horiba B-743 (mid range, general purpose)	$345.00 (unit price)
Replacement sensor	$145.00 (unit price)
Standard Solutions	$40.00 (unit price)
Miscellaneous costs	$50.00 (unit price)
Total NO_3^--N on ISE	**$0.58**[b] (per sample)

[a]Mean based on inquiries at 11 commercial laboratories in the United States.
[b]Based on a mean of 1500 readings per sensor (three readings per sample).
Note. Numbers in bold indicate total costs per sample for the three methods.

analysis on an ISE is roughly U.S. $0.58 (USD), nearly 66 times less expensive than sending samples for analysis in country ($39USD) or shipping them to the USA for analysis in a commercial laboratory ($37USD; Table 2).

The ISE correlated very strongly with the colorimetric method and shows an improvement on an initial study ($r^2 = 0.87$; Hartz et al. 1993). Such initial studies, however, were conducted on solutions with low concentrations NO_3^--N (0.02–1 mg NO_3^- L^{-1}), far less than concentration range leaching from agricultural fields. These devices should be considered to be a standard method of NO_3^--N analysis on par with the cadmium-reduction method for water samples within 7 and 160 mg NO_3^--N L^{-1}. As the World Health

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Organization's current standard for NO_3^--N in drinking water is 10 mg NO_3^--N L^{-1}, the ISE can be used to monitor drinking water NO_3^--N concentrations in inaccessible regions.

These devices can improve both the spatial and temporal resolution of data on N dynamics as sensors are inexpensive and the lag time between collection and analysis is reduced. Finally, as these devices are easy to use, they put knowledge in the hands of those who need it most: agricultural extension agents and farmers. There is a great need for rugged, inexpensive, high-accuracy environmental sensors to build a scientific knowledge base that can keep pace with land-use and global climate changes.

Conclusions

Fertilizer use will increase in remote regions such as SSA as the African green revolution takes off. However, the environmental impacts of such a large-scale shift in management practices may be difficult to monitor using traditional methods because of the poor infrastructure for sample storage and chemical analysis. This study shows that an inexpensive, field-ready ISE can be used to accurately measure NO_3^--N in soil solution from agricultural fields receiving different levels of fertilizer inputs. The ISE, therefore, provides a method for measuring a critical component of the nitrogen cycle in a remote region on the brink of rapid land-use change.

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