Technical note: An open-source, low-cost system for continuous monitoring of low-concentration nitrate in soil and open water

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Abstract. Nitrate (NO_3^-), mainly leaching with soil pore water, is the primary nonpoint source pollutant of groundwater worldwide. Obtaining real-time information on nitrate levels in soils would allow gaining a better understanding of the sources and transport dynamics of nitrate through the unsaturated zone. However, conventional nitrate detection techniques (e.g. soil sample analysis) necessitate costly, laboratory-grade equipment for analysis, along with human resources, resulting in a laborious and time-intensive procedure. These drawbacks raise the need to develop cost-effective and automated systems for in situ nitrate measurements in field conditions. This study presents the development of a low-cost, portable, automated system for field measurements of nitrate in soil pore water and open water bodies. The system is based on the spectrophotometric determination of nitrate using a single reagent. The system design and processing software are openly accessible, including a building guide, to allow duplicating or changing the system according to user-specific needs. Three field tests, conducted over five weeks, validated the system's measurement capabilities within the range of 0-10 ppm NO_3^--N with a low RMSE of <0.2 ppm NO_3^--N when comparing the results to standard laboratory nitrate analysis. Data derived from such a system allow tracking of the temporal variation in soil nitrate, thus opening new possibilities for diverse soil and nutrient management studies.

1. Introduction

Nitrogen (N) is a macro-nutrient found in soil, groundwater, and open water bodies across the globe. Nitrogen is essential for crop production and applying nitrogen-based fertilizers is a common practice in agriculture. However, excess fertilization leads to low nitrogen use efficiency (NUE) and can cause groundwater contamination due to leaching of excess nitrate (NO_3^-) in the soil, which is the mobile form of nitrogen and is easily transported by water (Ascott et al., 2017; Turkeltaub et al., 2021; Levintal et al., 2023). Nitrate leaching from agricultural soils through the vadose zone has become the primary nonpoint source pollutant of groundwater (Ascott et al., 2017; Richa et al., 2022; Gurdak and Qi, 2012). Elevated

32 nitrate concentrations in open water, in addition to groundwater, are also considered a major threat

33 that can cause algae blooms and loss of aquatic life (Van Metre et al., 2016; Wherry et al., 2021).

34 Optimizing fertilization by applying the needed amount of nitrogen fertilizer for the crop at each growing

35 stage can reduce the environmental risks above. To achieve this, real-time information on soil pore water

36 nitrate levels is required (Yeshno et al., 2019), leading to a need for an accessible method to measure real-

37 time nitrate concentrations in soils. However, measuring continuous in situ soil pore water nitrate

38 concentrations is still a major environmental and agricultural challenge. During the last two decades,

39 different soil pore water nitrate characterization technologies were tested, including ion-selective

40 electrodes, portable spectrophotometers coupled with suction cups, and lab-on-a-chip technologies

41 (Bristow et al., 2022).

42 The majority of published nitrate sensing systems for soil pore water show promising directions, however,

43 they are limited to only lab tests, require complicated and repeated calibration procedures, or may be

44 considered as a proof-of-concept rather than a functional field system (e.g., Ali et al., 2019; Chen et al.,

45 2023; Tuli et al., 2009). Only two published studies, as far as we know, showed significant progress in

46 measuring soil pore water nitrate concentrations continuously in the field. Bristow et al. (2022) developed

47 ion-selective electrodes for soil nitrate sensing. The electrodes were field tested under a relatively high

48 nitrate measurement range of ~50-300 ppm NO_3^--N with a reported Root Mean Square Error (RMSE) of

49 ~16 ppm NO_3^--N. They described significant drift after eight weeks of field deployment that required the

50 development of a correction algorithm. In general, electrode fouling, drift, ion interference, limited

51 sensitivity, and the need for temperature compensation are major disadvantages of ion-selective electrodes

52 (Tuli et al., 2009).

53 Yeshno et al. (2019) presented a monitoring system for continuous measurements of nitrate concentrations

54 in soil pore water. Their system is based on ultraviolet (UV) absorbance spectroscopy to directly determine

55 nitrate without pretreatment of the sample, such as filtration or adding reagents. The system was tested at

56 four agricultural field sites during four sampling campaigns. The nitrate measurement range was ~10-350

57 ppm NO_3^--N (no RMSE was reported). The main advantage of the system is the durability and lack of

58 needed field calibration, thus we consider this system as the most advanced and robust solution for field

59 nitrate measurements currently available. Yet, the methodology is patented with no assembly details

60 provided, and therefore, it cannot be duplicated and deployed by other users.

61 This study describes the construction and performance of a portable, low-cost, automated system for pore

62 water nitrate measurements. The system is based on a spectrophotometer coupled with an array of pumps

63 and a suction cup installed in the soil. A comprehensive technical documentation encompassing system

64 design, assembly, programming, deployment, power management, and data analysis is included to allow

65 end-users to replicate, modify, and deploy the system to their specific requirements without requiring prior

66 engineering expertise. For validation, three field tests with a concentration range of 0-10 ppm NO_3^--N were

67 conducted over five weeks.

2. Materials and Methods

69 The system is based on the spectrophotometric determination of nitrate using a single reagent (Doane and

70 Horwáth, 2003). Each water sample is mixed with a reagent (Vanadium(III) chloride (VCl_3) +

71 Sulfanilamide + N-(1-naphthyl)ethylenediamine dihydrochloride (NEDD)) and then measured at 540 nm

72 wavelength. The absorption intensity is used to determine the nitrate concentration using a calibration curve

73 as detailed below.

2.1. Hardware

75 The field nitrate sensing system is established on the open-source hardware concept (Pearce, 2012, 2014)

76 and consists of three segments: the spectrophotometer, the hydraulics system, and the control unit (**Fig. 1a**).

77 The low-cost spectrophotometer is based on the design by Laganovska et al. (2020), utilizing the

78 C12880MA mini-spectrometer chip (Hamamatsu Photonics K.K., Japan). The device measures absorption

79 in the 450-750 nm range, yet we use only the 540 nm wavelength. The 3D-printed measurement box holds

80 the cuvette for sample measurements (**Fig. 1b**).

81 The hydraulics system consisted of six peristaltic dosing pumps, a set of 1/16" (1.57 mm) inner diameter

82 tubing, a 50 mL container for collecting the initial water sample (#1), a 15 mL container for mixing the

83 sample with the reagent (#2), a 50 mL container for post-processing waste collection of the sample mixed

84 with the reagent (#3), a reagent box (#4), and a ceramic suction cup used to collect the water samples from

85 the tested soil or water body (#5) (**Fig. 1a** and **1b**). The first pump (P1) is connected to the ceramic suction

86 cup for sample collection. The rest of the pumps work in coordination to mix the appropriate sample volume

87 with reagents, deposit it in the cuvette, and then clean the tubes and cuvette once the measurement is taken.

88 The spectrophotometer and hydraulics system are controlled using an open-source microcontroller

89 (Arduino Mega, Arduino, Italy) with a micro-SD card for data logging. The system is powered by a 12 V,

90 7 Ah battery connected to a 10 W solar panel. Hardware details, system assembly instructions, and pumps

91 sequence are provided on our GitHub page https://github.com/SahitiB/AGNET/tree/main.

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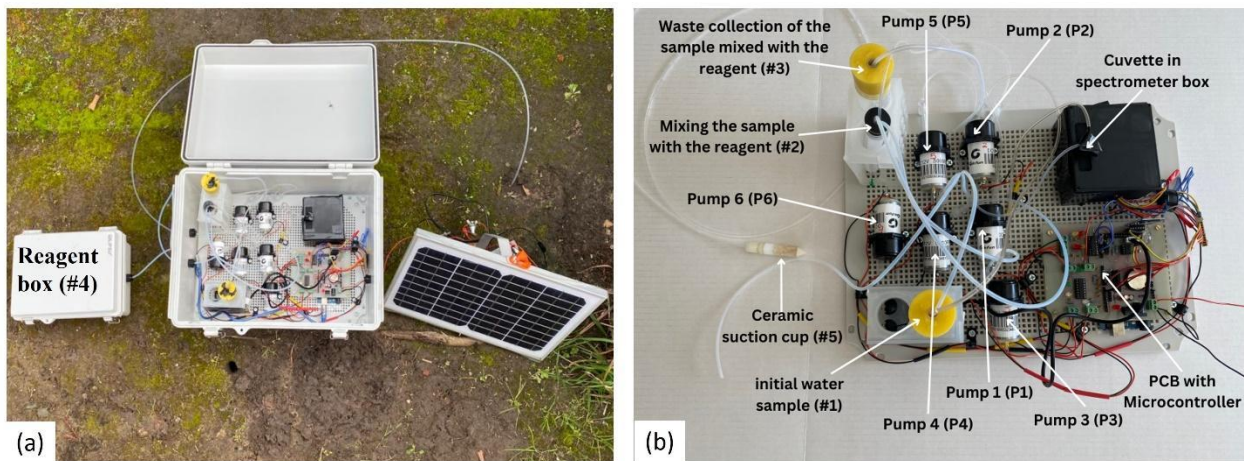
Figure 1. Experimental setting. The complete system during soil testing (a) and zoom in on the main box (b). We note that the spectrophotometer unit is based on the design by Laganovska et al. (2020).

2.2.   Software

An Arduino Mega microcontroller controls the device. Programming the Mega is done using C++, the default language of the Arduino Integrated Development Environment (IDE) (www.arduino.cc/en/software). The code contains the functions required to control the sequence of events for the entire system as well as the process of the spectrophotometer's results. The order and runtime of the pumps are controlled through the code and can be changed as needed. The complete code and open license conditions are described in our Github page https://github.com/SahitiB/AGNET/tree/main.

The flowchart in **Fig. 2** shows the sequence of a single nitrate measurement event, as instructed by the code. First, P1 pumps a soil pore water sample through the ceramic suction cup into container #1 until the water level sensor attached to the container is met at a sample volume of 5 mL. Then, P2 pumps 0.1 mL of the collected sample into container #2, followed by P4 pumping 0.9 mL of the reagent into the same container #2. The mixed sample is then transported to the cuvette (**Fig. 1b**, black box) using pump P3. Once the passive reaction time of 8 hr is completed, the spectrophotometer reading is taken and pumps P5 and P6 vacuum empty out the cuvette and container #1, and the entire system is thoroughly cleaned, emptied, and readied for the next cycle. The user can change the frequency between nitrate measurement events according to needs and battery consumption as detailed below.

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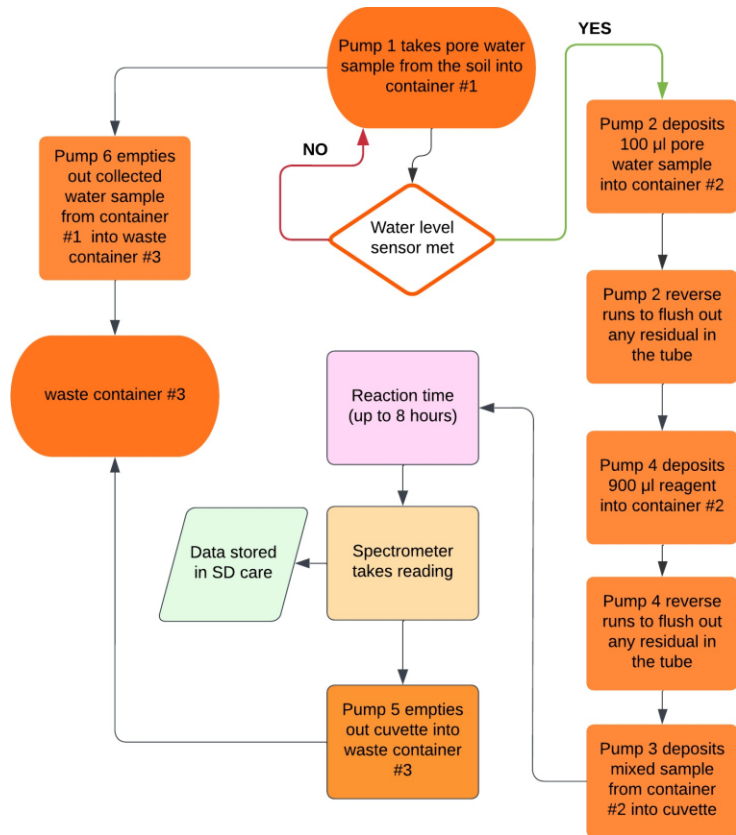
Figure 2. A flow chart of the main sequence in a single nitrate measurement event. A more detailed description for each step is given on our GitHub page.

2.3.   Field deployment

The system was calibrated using standard nitrate samples of 0, 0.1, 0.3, 1, 3, 5, 8, and 10 ppm NO_3^--N. After running those samples mixed with reagent through the spectrophotometer, a calibration curve (Beer-Lambert curve) is created relating the spectrophotometer absorbance values vs. the standard nitrate samples. A calibration curve is constructed before each experiment. Three field tests were conducted to evaluate system performance – two tests were run on soil pore water samples and one using open water samples. The tests were all carried out in Fremont, California, between February and June 2023. For each test, field-measured nitrate concentrations were compared against laboratory measurements with a Shimadzu 206-24000-92 UV/Visible scanning spectrophotometer at the University of California, Davis for validation. For the validation, sub-samples were directly taken from the water sample container (#1) after the pore water sample was obtained but before adding the reagent. Comparison of the field-measured nitrate with the standard laboratory method was done in several ways.

First, we conducted the variable test, which aimed at testing the accuracy of the system by randomly varying the amount of nitrate fertilizer in the soil during irrigation (Scotts Liquid Turf Builder with Plus 2 Weed

128   Control (25% nitrogen content), Scotts, USA). This tested the ability of the system to detect shifts in nitrate

129   levels. Secondly, a continuous test was performed to examine the system stability under rain conditions and

130   the ability to measure nitrate leaching in soil. The variable test ran for seven days with two readings per

131   day, and the continuous test ran for 17 days with one reading per day. In both tests, the suction cup was

132   installed at a depth of 6.3 cm (2.5 in) in the soil, and the system operated autonomously without any

133   maintenance. The third test was the open water pulse test to validate the ability of the system to measure

134   nitrate in water bodies (e.g., rivers and lakes). The suction cup was submerged in a 12 L water bucket for

135   12 days with one reading per day. Every fourth day, a 0.5 L cup of nitrate-based fertilizer (same as above)

136   was added to the water bucket to test the ability of the system to detect changes in nitrate levels in open

137   water. Atmospheric measurements for the experiments were taken from the California Irrigation

138   Management Information System station (CIMIS; station 171 Union City, CA).

139   **3.   Results and Discussion**

140   **3.1.   System performances**

141   A summary of the calibration and experimental results is presented in Table 1. One example of the Beer-

142   Lambert calibration curve is displayed in **Fig. 3**. The high R^2 of 0.998 between the absorption and the

143   standard nitrate samples validates the linearity of our spectrophotometer and the capability to accurately

144   measure nitrate.

145   **Table 1**. Summary of the calibration and experiment results

Experiment type	Duration and sampling rate [d]	Range of tested nitrate [ppm NO_3^--N]	Average RMSE [ppm NO_3^--N]
Calibration	One day	0-10	n/a
Soil variable test	Seven days (twice per day) 13/2/2023-19/2/2023	0-0.97	0.09
Soil continuous test	17 days (once per day) 28/2/2023-16/3/2023	0-2.39	0.10
Open water pulse test	12 days (once per day) 10/6/2023-21/6/2023	0-7.29	0.20

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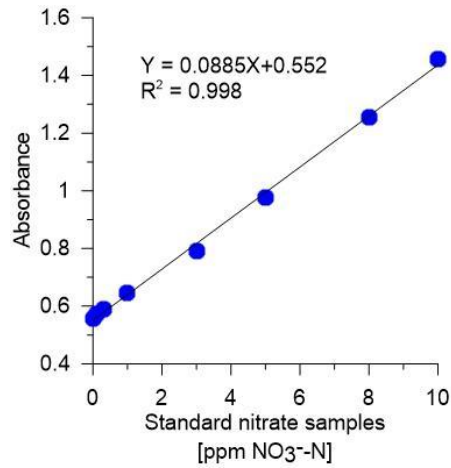
Figure 3. Beer-Lambert calibration curve for the system spectrophotometer using known standard nitrate concentrations of 0, 0.1, 0.3, 1, 3, 5, 8, and 10 ppm of NO_3^--N.

The first variable test focused on the low range of nitrate in the soil < 1 ppm NO_3^--N. During the seven-day test, the system was successful in measuring the changes in nitrate level with a RMSE of 0.09 ppm NO_3^--N compared to the lab reference analysis (**Fig. 4a**). We consider this as a low error value that validates our system in the low concentration range of nitrate. The soil continuous test showed similar high accuracy throughout the 17 days of trial with an average RMSE of 0.10 ppm NO_3^--N (**Fig. 4b**). The stability of measurements during this period suggests that no degradation of system performance was occurring with all measurement cycles conducted successfully. This 17-day test was conducted during a significant rain event with 12.2 mm d^{-1} of rainfall occurring on the first day. Therefore, we were able to measure, in real-time, the nitrate leaching in the topsoil (marked by the black curve line in **Fig. 4b**). The third test was conducted to validate the system in open water (**Fig. 4c**). In this case, the suction cup was submerged in a 12 L water container, and nitrate-based fertilizer was added every fourth day. RMSE remained low with 0.20 ppm NO_3^--N. The first step of water sampling using P1 was drastically faster compared to the soil tests, reducing the pump time from 30-40 min to 5-10 min per cycle.
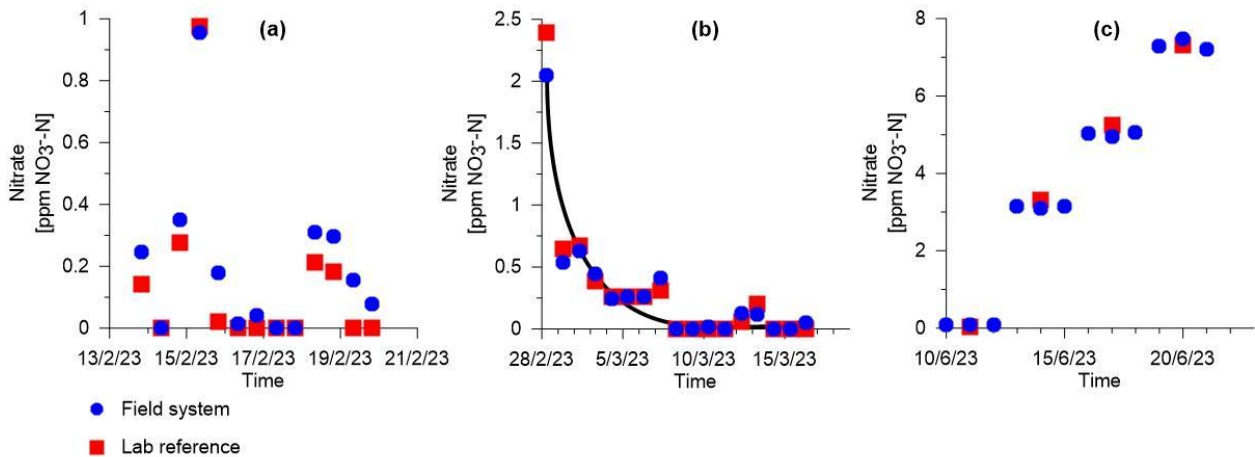
Figure 4. Experimental results of the spectrophotometer testing for the soil variable test of low nitrate concentrations (a), the soil continuous test under a rain event (b), and the open water pulse test (c). The black line in subplot (b) marks the nitrate leaching after a rain event of 12.2 mm d^{-1} on 28/2/2023. For each concentration level in the open water pulse test in subplot (c), three field measurements (blue dots) were compared to one laboratory measurement (red squares).

3.2.   System limitations and modifications

In this study, we presented and tested a portable, low-cost field nitrate sensing system to measure in situ nitrate concentrations in soil pore water and aquatic environments. Although the system is autonomous in terms of obtaining a sample and processing it until a nitrate concentration is determined, it does require some user input. The main user input required involves replacing the dry ice in the reagent box to maintain the recommended temperature of 4 °C for the Vanadium III Chloride reagent to work at its optimum (**Fig. 1a**). In our experiments, replacing the dry ice every five days was sufficient to ensure this temperature, however, all experiments were conducted at an average daily air temperature of 10 °C with a daily maximum of ~20 °C. Warmer conditions will require a more frequent replacement time of the dry ice or adding a cooler box or more advanced solutions, such as a small field refrigerated unit or a Peltier cooling plate based on solar panel or gas. Improving the reagent chill-box will increase system cost yet reduce human dependency. This, together with the addition of a low-cost modem or wireless communication such as Wifi or LoRa (Bristow et al., 2022; Sanchez-Iborra et al., 2018; Levintal et al., 2021), will make the device completely autonomous for weeks to months.

The system, considering our sample to reagent ratio, can accurately measure nitrate concentrations up to ~10 ppm NO_3^--N. This is a well-known limitation (Doane and Horwath, 2003) of using the Vanadium III Chloride reagent, which also exists in the lab. It would be possible to increase the range with the current system by either increasing the amount of reagent, decreasing the amount of sample, or both. However,

187 further experiments would be necessary to implement and test this extended range. When analyzing samples

188 with higher concentrations (70-80 ppm NO_3^--N), adding the reagent results in unusual colors (salmon,

189 orange, and yellow) that cannot be accurately measured and calibrated using known concentration standards

190 and the spectrophotometer. For example, a sample with a high concentration (e.g., approximately 120 ppm

191 NO_3^--N) will turn yellow and the spectrophotometer will register absorbance corresponding to

192 concentrations lower than 1 ppm NO_3^--N, indicating a false reading. A possible solution could be the

193 addition of a visual color sensor to notify the user when the color is exceeding the concentration range

194 covered by the standard (i.e., high nitrate concentrations) to then dilute the sample accordingly. This will

195 require changing the design of the system and adding a dilution mechanism.

196 If a high measurement frequency is required, a heating device can be added, or a temperature curve can be

197 developed to reduce the 8-hour reaction time of the Vanadium III Chloride reagent in the cuvette. Yet, this

198 need is highly site-specific as warmer climates will reduce the sample-reagent time naturally. Higher

199 measurement frequency means higher power consumption, which should be optimized using a larger

200 battery capacity and/or a larger solar panel. In our experiments, taking the soil variable test as a reference

201 (**Fig. 4a**), the 12 V, 7 Ah with a 10 W solar panel was sufficient for two samples per day for seven

202 continuous days. This was achieved under cloudy skies with an average daily solar radiation of 156 W m^{-}

203 ^{2}. Power consumption is site-dependent due to the variability in the solar panel's efficiency to charge a 12

204 V battery, and moreover, due to the changes in soil moisture. Lower soil moisture will increase the run time

205 of the peristaltic pump extracting the water sample from the soil (P1 in **Fig. 1**), therefore increasing power

206 consumption for each nitrate sampling cycle. In very dry conditions, water samples cannot be extracted

207 from the soil and the system will not work. A possible optimization solution could be the addition of a soil

208 moisture sensor to deactivate the system under very dry conditions. We note that this is a common problem

209 of using suction cups in dry soils unrelated to this specific system.

210 This study demonstrates the capabilities to measure nitrate leaching during a rain event and nitrate changes

211 in open water. Additional potential research objectives for the low-cost portable nitrate system include: (1)

212 measuring soil nitrate levels in the root zone of an agricultural field during a growing session to optimize

213 nitrogen fertilization applications, i.e., precision agriculture methods to reduce groundwater pollution

214 (Yeshno et al., 2019). This application will need to include a soil moisture sensor to allow the calculation

215 of the nitrate stock available for plant uptake (Bristow et al., 2022); (2) couple the system with low-cost

216 oxygen sensors (Levintal et al., 2022) to investigate in real time the occurrence of denitrification and its

217 dependency on soil oxygen levels (Levintal et al., 2023); (3) measure nitrate changes in lakes/rivers during

218 heavy rain events or floods, and (4) implementing the same design to measure other contaminants in the

219 soil pore water and open water given that they have distinct absorbance in the range of our
220 spectrophotometer of 450-750 nm.

221 **4. Summary**

222 This study presents the development of a low-cost, portable, automated system for field measurements of
223 nitrate in soil pore water and open water bodies. The system consists of an Arduino-controlled array of
224 pumps, a suction cup installed in the soil, and a spectrophotometer that measures the nitrate concentration
225 after the water sample is mixed with a reagent. Three field tests conducted over five weeks to validate the
226 system within a measurement range of 0-10 ppm NO_3^--N showed a low RMSE of <0.2 ppm NO_3^--N when
227 comparing the results to standard laboratory nitrate analysis. This nitrate range is suitable for soils with low
228 nitrate concentrations or open water. The system design and processing software are openly accessible. By
229 designing a system in which all electronics are limited to buyable hardware components and the files for
230 the printed circuit board (PCB) are provided, it is possible to duplicate or change the system according to
231 user-specific needs. The total cost of the system components is USD $1,100, excluding reagents, which we
232 hope will allow reproducibility and open new possibilities for conducting field studies in soil and
233 environmental nitrate monitoring.

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Code and data availability

The complete technical guide and code are available in our GitHub repository (https://github.com/SahitiB/AGNET/tree/main)

Author contributions

EL conceptualized the study and designed the system, SB constructed the system and conducted the study, SB and EL wrote the first manuscript draft, HED provided the resources and project supervision. All the authors (SB, CPG, HED, and EL) contributed to the final version.

Competing interests

The contact author has declared that none of the authors has any competing interests.

Acknowledgments

This research has been supported by the Gordon and Betty Moore Foundation (grant no. 7975), the United States–Israel Binational Agricultural Research and Development Fund (Vaadia-BARD Postdoctoral Fellowship no. FI-605-2020), and the USDA National Institute of Food and Agriculture grant no. 2021-68012-35914.

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