Technical note: An open-source, low-cost system for continuous monitoring of low-concentration nitrate ~~monitoring~~ 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

32 source pollutant of groundwater (Ascott et al., 2017; Richa et al., 2022; Gurdak and Qi, 2012). Elevated

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

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

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

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

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

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

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

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

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

42 (Bristow et al., 2022).

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

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

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

46 2023; Tuli et al., 2009). Only two published studies, as far as we know, showed significant progress in

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

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

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

50 ~16 ppm NO_3^--N. They described significant drift after eight weeks of field deployment that required the

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

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

53 (Tuli et al., 2009).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

68   conducted over five weeks.

69   **2.   Materials and Methods**

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

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

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

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

74   as detailed below.

75   **2.1.   Hardware**

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

91   7 Ah battery connected to a 10 W solar panel. Hardware details, system assembly instructions, and pumps

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

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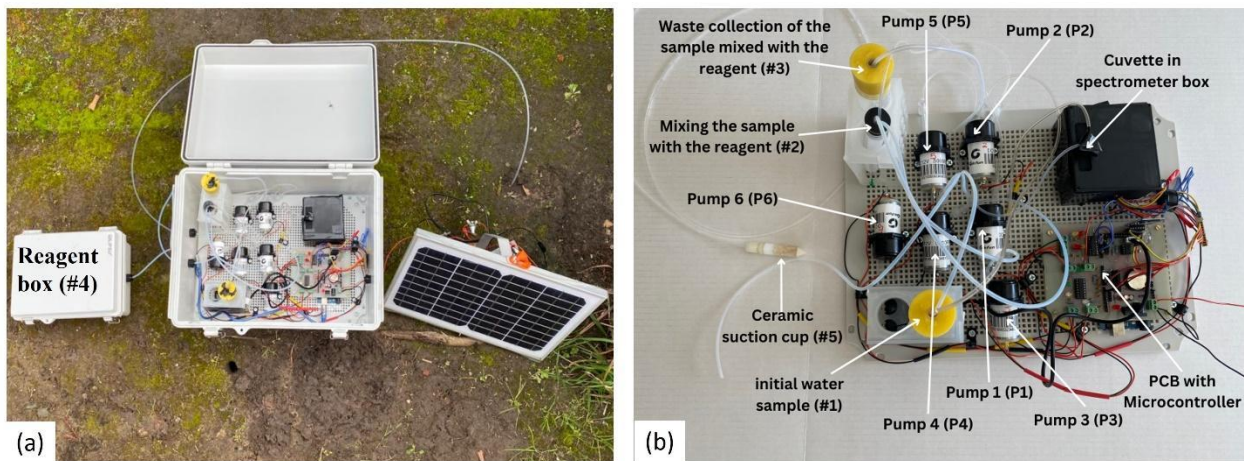
94 **Figure 1**. Experimental setting. The complete system during soil testing (a) and zoom in on the main box

95 (b). We note that the spectrophotometer unit is based on the design by Laganovska et al. (2020).

96 **2.2. Software**

97 An Arduino Mega microcontroller controls the device. Programming the Mega is done using C++, the

98 default language of the Arduino Integrated Development Environment (IDE)

99 (www.arduino.cc/en/software). The code contains the functions required to control the sequence of events

100 for the entire system as well as the process of the spectrophotometer's results. The order and runtime of the

101 pumps are controlled through the code and can be changed as needed. The complete code and open license

102 conditions are described in our Github page https://github.com/SahitiB/AGNET/tree/main.

103 The flowchart in **Fig. 2** shows the sequence of a single nitrate measurement event, as instructed by the code.

104 First, P1 pumps a soil pore water sample through the ceramic suction cup into container #1 until the water

105 level sensor attached to the container is met at a sample volume of 5 mL. Then, P2 pumps 0.1 mL of the

106 collected sample into container #2, followed by P4 pumping 0.9 mL of the reagent ~~(Vanadium III Chloride)~~

107 into the same container #2. The mixed sample is then transported to the cuvette (**Fig. 1b**, black box) using

108 pump P3. Once the passive reaction time of 8 hr is completed, the spectrophotometer reading is taken and

109 pumps P5 and P6 vacuum empty out the cuvette and container #1, and the entire system is thoroughly

110 cleaned, emptied, and readied for the next cycle. The user can change the frequency between nitrate

111 measurement events according to needs and battery consumption as detailed below.

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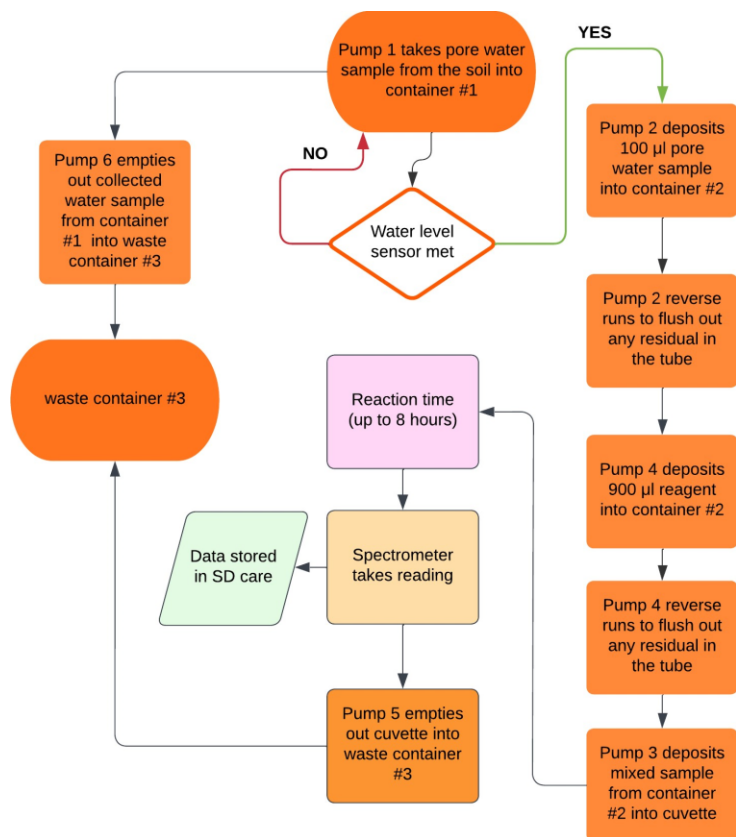
Figure 2. A flow chart of the main sequence in a single nitrate measurement event. A more detailed description for each step is given on our GitHub page.

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

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

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

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

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

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

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

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

136   12 days with one reading per day. Every fourth day, a 0.5 L cup of nitrate-based fertilizer (same as above)

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

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

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

140   **3.   Results and Discussion**

141   **3.1.   System performances**

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

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

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

145   measure nitrate.

146   **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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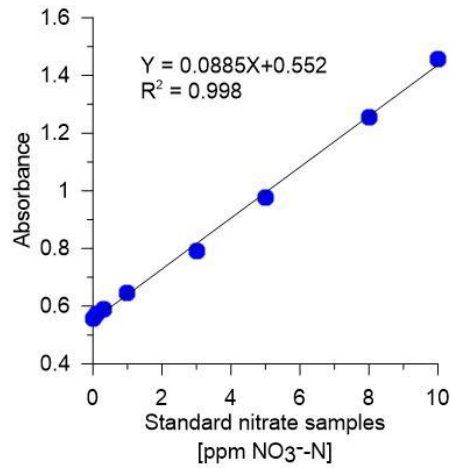
Figure 3. Beer-Lambert calibration curve for the system spectrophotometer using known standard nitrate concentrations of 0, 0.1, 0.3, 1, 3, 5, 8, and 10 ppm of NO_3^--N.

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.

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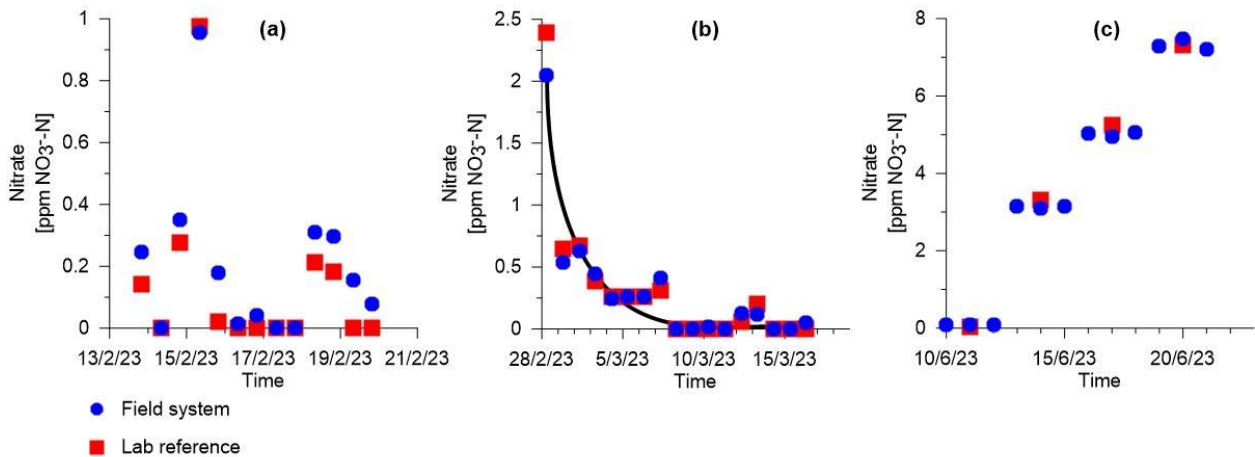
Figure 4. Experimental results of the spectrophotometer testing for the soil variable test of low nitrate concentrations (a), the soil continuous test under a rain event (b), and the open water pulse test (c). The black line in subplot (b) marks the nitrate leaching after a rain event of 12.2 mm d^{-1} 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~~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,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

204 ^{2}. Power consumption is site-dependent due to the variability in the solar panel's efficiency to charge a 12

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

220   soil pore water and open water given that they have distinct absorbance in the range of our

221   spectrophotometer of 450-750 nm.

222   **4. Summary**

223   This study presents the development of a low-cost, portable, automated system for field measurements of

224   nitrate in soil pore water and open water bodies. The system consists of an Arduino-controlled array of

225   pumps, a suction cup installed in the soil, and a spectrophotometer that measures the nitrate concentration

226   after the water sample is mixed with a reagent. Three field tests conducted over five weeks to validate the

227   system within a measurement range of 0-10 ppm NO_3^--N showed a low RMSE of <0.2 ppm NO_3^--N when

228   comparing the results to standard laboratory nitrate analysis. This nitrate range is suitable for soils with low

229   nitrate concentrations or open water. The system design and processing software are openly accessible. By

230   designing a system in which all electronics are limited to buyable hardware components and the files for

231   the printed circuit board (PCB) are provided, it is possible to duplicate or change the system according to

232   user-specific needs. The total cost of the system components is USD $1,100, excluding reagents, which we

233   hope will allow reproducibility and open new possibilities for conducting field studies in soil and

234   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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