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Interactive comment on "A novel analytical approach for the simultaneous measurement of nitrate and DOC in soil water" *by* Elad Yeshno et al.

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Interactive comment on "A novel analytical approach for the simultaneous measurement of nitrate and DOC in soil water" by Elad Yeshno et al.

Anonymous Referee #2 Received and published: 6 October 2020

General comments: This paper presents an advance in the analysis of soil water. Maybe not a giant leap but surely an interesting technique. The text is understandable and ïnËĞCuent and the reader is able to get a fairly complete idea of the work done. However, some important points should be discussed.

We would like to thank the reviewer for the time and effort made in evaluating our paper, and we will do our utmost to explain the methods presented in this work, and answer the reviewer questions.

Comment 1: How easy is it for the farmer to prepare samples for analysis in a reproducible way?

Reply to general comment 1: It was not within our intentions that the farmer would be dealing with the dilution and spiking process described in the methods chapter. The purpose of this process is to obtain a matrix of samples with various DOC and nitrate concentrations which can be then used in the calibration process in a method for estimating nitrate concentration. This method can then be the analytical core for a LED-based nitrate sensor. Since this process requires previous knowhow and skills, the tasks of installation and calibration of such sensor would be done by a trained personal and not by the farmer. The only role of the farmer in such model is to send a porewater sample or soil samples to whom which providing the soil sensing facilities, and the sensor installation and calibration. Once the installation and calibration processes are completed the farmers will be able to use the calibrated probe for long durations without any further analysis. The calibration process was found to be robust enough to enable direct measurements. Yet, a site-specific it requires pre-calibration.

Comment 2: No explanation is given on how the estimation of ïn ËŻAgure 5 has been obtained.

Reply to general comment 2: Figure 5 presents predicted nitrate concentrations plotted against observed nitrate concentrations. The absorbance data used to calibrate the predicted nitrate concentration was measured at 235 nm by a standard laboratory spectrometer. Similar data is presented in figure 3, however, in this case, absorbance data were collected at 300 nm. Currently, 300 nm UV LED are readily available and can be used to perform nitrate analysis, as presented in this paper. However, the results presented in figure 5 demonstrates how a significant increase in the quality of the nitrate analysis can be obtained when calibration is carried at 235 nm. As such, we believe that once 235 nm LED would become commercially available, it can greatly increase the accuracy of such sensor. We have revised the manuscript (lines 228-237) and figure 5 caption to make the addressed issue clearer.

Specific comments:

Comment 1: The authors state that "the polynomial calibration equation for ËĞ nitrate must be site-speciïn ËŻAc.". This can be a limitation to a system that should be ËĞ used by "farmers who are focused on food production in large scale agricultural setups".

Reply to comment 1: It is indeed correct that the calibration is a site-specific feature. However, since it is mainly affected by the composition of the DOC which is driven by the parameters such as soil type, climate conditions, fertilization methodology, source of organic matter, and other environmental aspects of the site. Therefore, the calibration made for a monitoring system that is installed under a field will continue to represent the site for a long duration. It may change only upon a dramatic change in the field conditions such as adding significant organic matter from a different source. In such a case the system may be recalibrated without the need to take it out of the soil. Moreover, preliminary research made when calibrating the system for a single point in a crop field shown that the calibration was accurate for measuring nitrate at porewater taken in other points of the crop field as well. This data is under preparation and we hope to publish it soon. Note that lengthy field observations of nitrate measurement by spectral analyses when reduction of DOC interference was done by a site-specific algorithm, showed that once calibration was obtained it remained valid for a prolonged time interval (2 years) (Yeshno et al., 2019). This implies that the chemical composition of the DOC and thus its spectral interference in the UV range fairly stable over time, and as such allow continuous reading of nitrate by spectral techniques.

Comment 2: Five soil samples can be few to represent all possible real situations.

Reply to comment 2: We agree with the reviewers comment; we indeed intend to extend this research in order to map as many possible soils and investigate the connection between DOC type to compost type, soil type, and the DOC optical characteristics. However, this research was design to serve as a proof of concept, and as such, we chose six types of soil that would represent a large variety of agricultural soil types: (1) an open crop field with sandy loam soil located near the coastal plain (2) an inland open crop field with clay soil (3) a conventional vegetables greenhouse with sandy loam (4) an organic vegetables greenhouse with loamy soil (base on compost fertilization) (5) citrus orchards with loamy soil and (6) a general case of sandy loam mixed with commercial humus. A table was added to the manuscript (Table 1 – line 395) to present each study site location and soil type.

Comment 3: What is the accuracy of the value of Table 1?

Reply to comment 3: The average error value for the DOC and the nitrate is 0.1% and 6% respectively. The standard error values were added to the nitrate and DOC concentrations presented in table 2 (line 396), as well as to the data found in the supporting information file.

Comment 4: The authors state that "An important advantage of DOC ïnËĞCuorescence spectroscopy is that it is not affected by the presence of nitrate in ′ the solution." Sure? Why?

Reply to comment 4: Although nitrate and DOC have some similar absorption characteristics in the UV spectrum, only DOC has the chemical structural complexity which comprises the aromatic rings required to have fluorescence characteristics at the UV range. It is therefore that UV fluorescence spectroscopy is commonly applied for analyzing DOC in samples containing dissolved nitrate or iron instead of absorbance spectroscopy techniques (Bridgeman et al., 2011). The manuscript had been revised to clarify the addressed issue (lines 150 - 155)

Comment 5: It would have been better a version of Figure 3 where the nitrate prediction is based on the DOC measurement made with the ïnËĞCuorescence ′ technique.

Reply to comment 5: It is indeed possible to plot the estimated nitrate concentration in figure 4 (y-axis), by plugging in the predicted DOC concentrations in the nitrate site-specific polynomial equation. However, for technical issues, some of the data used to make the DOC calibration curves presented in figure 4 is not compatible with the data used to plot the observed vs predicted nitrate concentrations in figure 3. Still, the quality of correlation found between the fluorescence intensity to the DOC concentration is very high, with R2 no lower than 0.99 (Figure 4). Thus, predicted nitrate concentration calculated from DOC concentration obtained by fluorescence would be almost similar to predicted nitrate concentration calculated for known DOC concentration. We can however still exemplify this resemblance in the predicted nitrate concentrations for two cases: (1) citrus's orchard, and the (2) conventional greenhouse, where a sufficient amount of compatible DOC/nitrate data existed (Figure 1 at the current file).

Comment 6: Please explain why only the points of ïn ËŻAgure 3b are vertically aligned.

Reply to comment 6: We would like to deeply thank the reviewer for revealing a mistake in one of our data files. a thorough exam had exposed a typing mistake at an excel spreadsheet which had caused an error in the data plotted in figure 3b. We have corrected the figure and the supporting information file accordingly. Consequently, the data points in figure 3b should not normally appear vertically aligned.

Comment 7: Technical corrections the correct spelling is "humus" and not "hummus". Line 168, "Figure 3" is again "Figure 2".

Reply to Comment 7: comment accepted. The main manuscript, figures, figures caption, and supporting information files had been revised accordingly.

Comment 8: Line 172, "x" should be the multiplication sign

Reply to comment 8: comment accepted, the manuscript at Line 186 had been revised.

References:

Bridgeman, J., Bieroza, M. and Baker, A.: The application of fluorescence spectroscopy to organic matter characterisation in drinking water treatment, Rev. Environ. Sci. Biotechnol., 10(3), 277–290, doi:10.1007/s11157-011-9243-x, 2011.

Yeshno, E., Arnon, S. and Dahan, O.: Real-time monitoring of nitrate in soils as a key for optimization of agricultural productivity and prevention of groundwater pollution, , (2009), 3997–4010, 2019.

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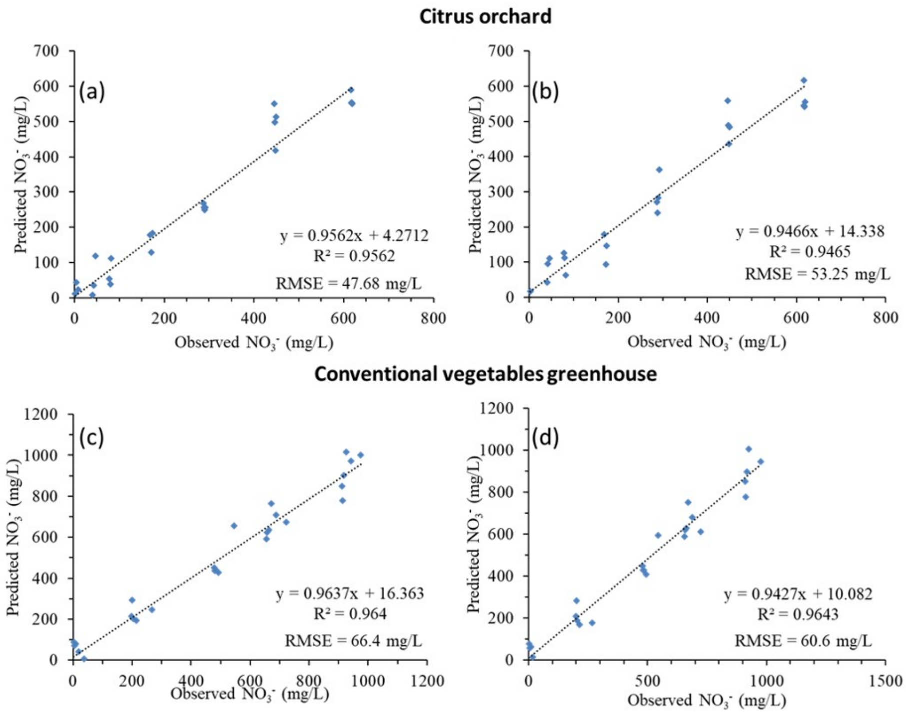

Figure 1 – Predicted vs. observed nitrate when predicted nitrate is estimated for: DOC values obtained by standard laboratory TOC analyzer (a&c) and DOC values obtained by fluorescence spectroscopy (b&d) for the case of the citrus orchard and the conventional greenhouse.

Fig. 1.

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Discussion paper