Hydrol. Earth Syst. Sci. Discuss.,
https://doi.org/10.5194/hess-2020-417-AC3, 2020

Hydrology and Earth System Sciences
Discussions
Open Access
EGU

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

Elad Yeshno et al.

eladyes@post.bgu.ac.il

Received and published: 3 December 2020

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 #3

Received and published: 20 October 2020

The Manuscript "A novel analytical approach for the simultaneous measurement of nitrate and DOC in soil water" by Elad Yeshno et al. presents a measurement setup which tests a combination of two analytical tools to demonstrate the potential of wavelength

Printer-friendly version

Discussion paper

specific detection of soil water nitrate concentrations in carbon rich soils. The Authors present in a very straightforward manner what they have done due to which reasons and how the outcomes support the choice of the combined measurement techniques presented in this paper.

The authors applied a combination of UV absorption spectrometry (around 300 nm) with fluorescence spectrometry (excitation/emission at 350/451 nm) to demonstrate the possible feasibility of this setup when applied with single banded LED technology. The study seems to be embedded in a research project or development program, which delivered already an interesting publication with regard to a possible application of the method (Yeshno et al. 2019, HESS (within the reference list this citation misses the journal. However, I have some points that need to be discussed prior to the editors decision about a possible publication in HESS.

Authors reply:

We would like to thank the reviewer for investing the time and effort needed to evaluate the work carried during this research. We however like to clarify that this research presents an analytical concept to estimate nitrate concentration in soil porewater containing Dissolved Organic Carbon (DOC). Furthermore, as this paper purely focuses on the conceptual level, it does not present a new measurement setup. As such, the results presented in the paper merely implies the possibility of using this concept as a ground for the development of a UV LED-based nitrate sensor. âĂČ Comments:

Comment 1: Generally, as a reader I would really appreciate the demonstration of a (-n inexpensive) LED-based technology which is able to directly measure in-situ soil water concentrations of DOC and nitrate. But it needs to be discussed whether a feasibility study for the application of analytical tools fits into the scope of HESS or better into another journal format (e.g. the EGU Journal “Geoscientific Instrumentation, Methods and Data Systems”). Reply to comment 1: Since the goal of the presented research was to provide a proof of concept for a new analytical approach, we have conducted the

experiments using standard laboratory equipment. However, we believe that the results presented in this study about the relation between DOC, nitrate and their absorbance characteristic can be the base for the development of an affordable, LED-based sensor. As such the future development may be of high interest for scientists from the fields of hydrology and environment.

Comment 2: The presentation of the study does not follow the typical/expected structure and misses some details: While the introduction section describes the background of the research problem and the linkage between DOC and Nitrate UV-absorption, it misses a review of other methods applicable to the problem presented in the paper. The interference of UV absorption of nitrate and DOC is known and several studies (some of them are cited in the paper, but in a different context) use two different wavelengths within the UV spectrum in combination with statistical models to overcome this problem. Even several commercial UV-Vis spectrometers for a parallel direct measurement of DOC and nitrate in aqueous solution are available on the market and widely in use e.g. in monitoring stations in wastewater treatment plants. The principle of this approach is at least similar to the one applied within this study and could be transferred to an application with LED-technology, likewise. The authors should explain how their approach improves the current state of the art technology (in their approach a second analytical tool is required).

Reply to comment 2: Indeed, there are few common and standard methods to deal with the interference to nitrate estimation caused by the UV absorption of DOC, however, to the best of our knowledge non were successfully tested for a range of concentrations of nitrate present in the porewater of agricultural root zone (Nitrate concentrations ranging from tens to thousands mg/L and DOC from tens to hundreds mg/L). For example, Ferree and Shannon, (2001) presented such method based on second derivative absorption spectroscopy for DOC in concentration up to 77 mg/L. However, this method is limited for N-nitrate concentration higher than 10 mg/L. An additional, similar method is carried by calibrating the nitrate concentration to reduction of twice the absorbance

Printer-friendly version

Discussion paper

intensity at 275 nm from the absorbance at 220 nm (Armstrong, 1963). However, this method can only be used when the absorbance at 275 nm is lower than 5 % of the absorbance measured at 220 nm. A further method that can be used to reduce interference from DOC is relying on a wide range absorbance measurement of the UV-VIS spectrum, combined with statistical tools, such as the Partial Least Square Regression (PLSR) (Avagyan et al., 2014; Etheridge et al., 2014; Rieger et al., 2006). Yet, a primary goal in this research was to develop a method that would serve as the basis for an affordable LED-based sensor for nitrate. Yet, the PLSR method, which requires UV-VIS absorption data at a broad spectrum cannot be used as a base for a narrow band, LED-based sensor. Lastly, none of the presented methods mentions the necessity for site-specific calibration. As shown previously in a research made by the author of this paper, due to the variability in the optical absorption characteristics of the DOC found at different agricultural sites, a site-specific calibration is required to perform adequate calibration for nitrate (Yeshno et al., 2019). The method described is based on preliminary sample chemical analyses of the DOC found in each site porewater, and obtaining a calibration equation that is dealing with the absorption/fluorescence characteristic found at each study site.

Comment 3: The description of the methodology regarding sampling and analytical procedures is very clear and to the point. The method development, e.g. the derivation of the 2D Model, which is then applied to the data, is presented within the result & discussion section. Here I would expect a clear difference between method description and acquired parameter values. As mentioned by reviewer 2, I would have expected a larger data set, covering a broader range of possible DOC concentrations than 6 and 25 ppm DOC, respectively.

Reply to comment 3: The comment is accepted and the part of the methods that is dealing with the sample preparation has been moved to the results section (lines 172-181). Regarding the presented data set, figure 1 merely presents an example leading the reader into the complexity of the superposition of the absorption spectroscopy caused

by the DOC and nitrate presence in the solution. We have calibrated and tested the concept for a broad DOC concentrations range, varying between 6 – 213 mg/L (table 1). Additional data of the DOC concentrations range tested in this research can be seen under section S2 in the supporting information file.

Comment 4: The specific results and the quality of the presented method are not presented in detail. In addition to the figures, there is only an overall description of the correlations between predicted and measured nitrate concentrations as well as the total range of RMSE. Since this is a new methodological setup, I would have expected at least a table, where the quality differences for the different field sites with regard to the differences in background DOC concentrations is presented to the reader.

Reply to comment 4: We accept the comment and a table of RMSE, R2, P-value, and DOC / Nitrate concentrations range had been added to the manuscript (table 4 line 402).

Comment 5: The discussion section does not compare the acquired results to other studies in the field (the authors present not a single citation of other literature from the field within this section).

Reply to comment 5: indeed, the discussion section does not compare the acquired results to other studies in the field, since it is not found necessarily in a comparable manner. As described in detail under comment 2, most of the standard commonly applied absorbance spectroscopy techniques are limited to 10 mg/L N-nitrate and to about 80 mg/L of DOC. These techniques are mostly suitable for laboratory analyses were dilutions of the obtained water samples can be made. Yet, since the current research focuses on porewater found in cultivated soils, we were expecting concentrations range higher in two orders of magnitude of nitrate and DOC. Additionally, these methods do not provide a site-specific solution to the local chemical and optical characteristics of the DOC. It is therefore that results obtained from the commonly used methods cannot be directly compared to the results found in this paper.

Comment 6: Since the presented method needs a site-specific calibration (comparable to the UV-vis-approach), the advantage of this method over others is not clear to me, e. g. whether this setup provides a higher accuracy than UV-vis based spectrometers. Overall, I recommend major revisions.

Reply to comment 6: The presented methods require site-specific calibration, to overcome the interference on the nitrate's absorbance spectrum, caused by the local DOC chemical composition in the soil. As shown in the previous work of Yeshno et al., (2019) the optical characteristics of DOC may differ from site to site, and as such compensation of interference from DOC cannot be associated only with its concentration and should account for its local chemical and optical characteristics as well. Most of the known standard, common methods to deal with the absorption caused by DOC (as detailly described under reply to comment 2 and comment 5) do not provide a site-specific solution for the local DOC, and as such was less suitable for in-situ, porewater analyses. Nevertheless, although statistical-based analyses such as PLSR and PLA shows potential for in-situ porewater analyses for nitrate, this method requires absorbance data on a broad spectrum of the UV-VIS light. As such, these methods are less suitable as an analytical core for the development of an LED-based sensor. Nevertheless, as discussed in the reply to comment 1 of reviewer #2, once the system is calibrated throughout the process of installation, the calibration curve may be relevant for long durations (years). Moreover, if needed the system can be recalibrated again (or from time to time) without the need to take the system out of the soil.

References:

Armstrong, F. A. J.: Determination of Nitrate in Water by Ultraviolet Spectrophotometry, Anal. Chem., 35(9), 1292–1294, doi:10.1021/ac60202a036, 1963.

Avagyan, A., Runkle, B. R. K. and Kutzbach, L.: Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas, J. Hydrol., 517, 435–446, doi:10.1016/j.jhydrol.2014.05.060, 2014.

Etheridge, J. R., Birgand, F., Osborne, J. A., Osburn, C. L., Burchell, M. R. and Irving, J.: Using in situ ultraviolet-visual spectroscopy to measure nitrogen, carbon, phosphorus, and suspended solids concentrations at a high frequency in a brackish tidal marsh, Limnol. Oceanogr. Methods, 12(1 JAN), 10–22, doi:10.4319/lom.2014.12.10, 2014.

Ferree, M. A. and Shannon, R. D.: Evaluation of a second derivative UV/visible spectroscopy technique for nitrate and total nitrogen analysis of wastewater samples, Water Res., 35(1), 327–332, doi:10.1016/S0043-1354(00)00222-0, 2001.

Rieger, L., Langergraber, G. and Siegrist, H.: Uncertainties of spectral in situ measurements in wastewater using different calibration approaches, Water Sci. Technol., 53(12), 187–197, doi:10.2166/wst.2006.421, 2006.

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. Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2020- 417, 2020. C3

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2020-417, 2020.

Printer-friendly version

Discussion paper