

June 10, 2019

A review of: Continuous in-situ monitoring nitrate concentration in soils – a key for groundwater protection from nitrate pollution. By Yeshno et al.

### **Summary and recommendation**

This manuscript describes the development and first successful implementations of a new apparatus for real-time monitoring of soil-pore-water nitrate concentration. The apparatus is based on a customized suction cup and tubing with a small “dead volume” that can hold continuous flow to an optical flow-cell in which the pore-water are exposed to a UV lamp and absorbance is measured by a spectrophotometer, the pore-water continue to flow nfrom the optical cell to a sample collector for lab analysis and calibration. A site-specific optimization of the working wave-length which consider the interference with dissolved organic carbon (DOC), the sensitivity of the absorbance to nitrate concentration and the correlation between them, is described. Site specific calibration was validated with samples from the same in-situ suction cups at 3 occasions within 2 years after the calibration samples. Monitoring nitrate in controlled tracer experiments in columns with different soils was shown to be comparable to nitrate lab-analysis of corresponding pore water samples. The suggested apparatus looks as a large step towards monitoring root zone nitrate / controlled N fertilization systems in agricultural fields. These type of systems can enhance N fertilization efficiency and reduce nitrate leaching to groundwater, significantly (nitrate is the no. 1 contaminant leading to disconnection of wells from direct supply to drinking water systems). Therefore I defiantly recommend publication in HESS after some clarifications and modifications listed below.

### **General comments**

- 1) Continuous suction of pore-water from unsaturated porous medium (and bringing it up to surface in small diameter tubing) must impose some limitations of minimum water-content (soil-texture dependent) in which this apparatus can work (what suction pressures are imposed on the cups?). A TDT for water content monitoring was installed in the experimental setup, therefore I am sure the authors have some understandings considering the soil moisture conditions effects on the nitrate monitoring possibilities that are of interest for the HESS readership. Therefore I encourage the authors to elaborate on this issue.
- 2) The use of the term “absorbance intensity” throughout the text, figures and supplements instead of absorbance is somewhat inadequate. Absorbance is defined as the log of a ratio of light intensities. Change throughout.

### **Specific comments**

- 1)L 20 “untreated” do you mean non-disturbed?
- 2)L 40 I would suggest to enhance the arguments for this type of monitoring saying: Nitrate uptake was observed and modeled as passive uptake with a threshold root-zone concentration ( $C_{max}$ ) from which the roots can up take only  $S \cdot C_{max}$  ( $S$  - root water uptake, e.g. Simunek and Hopmans, 2009 (Ecological Modeling)). This mechanism

imposes a jump in deep leaching of nitrate at times when  $C > C_{max}$ , hence monitoring of nitrate concentration can serve as controller leading to increasing N use efficiency and decreasing groundwater contaminations. Values of  $C_{max}$  for different crops were reported between 20 to 45 mg/l NO<sub>3</sub>-N, (Kurtzman et al., 2013; Levy et al., 2017 (HESS)).

3) L 90 – “second derivative spectroscopy” is not a clear phrase for most of the hydrology readership. 1-2 sentences defining this term will help.

4) L 200 – With small sample size (4-7 points) it would help to add to the R<sup>2</sup> values also the P values of the slopes of the regression models, to enhance the sense of their significance.

5) L238, L240 “1.3 m” should be 1.3 m below surface or a depth of 1.3 m. Same for 13.3 m.

6) L310. I would start this paragraph with something like :

A high R<sup>2</sup> can be achieved also with wavelengths in which the sensitivity of the absorbance to nitrate concentration is extremely high and absorbance could not be used for estimating nitrate concentrations. Therefore the variance of the absorbance values that correlate well with the range of nitrate concentrations is a second criteria for choosing the best wavelength.

Starting the paragraph with “Variance..” is ambiguous.

7) Figure 8 or L 337. Where are the calibration equations? Put them in the text or on the Figure.

8) L 417 delete “-based”.

9) Figure 9. It would be better not to use the calibration data (red points) in this analysis, and draw the predicted-observed regression lines (and R<sup>2</sup>) only for the validation points of the 3 later sampling dates. That would give a better estimation of the performance of the method.