

Reply to comments made by Referee #2 on the manuscript: “Continuous in-situ monitoring of nitrate concentration in soils – a key for groundwater protection from nitrate pollution” by: Elad Yeshno

We wish to thank the reviewer for its encouraging statement “*This method is unique and might change our ability to trace nitrate in soils*”. This is definitely the driving force for our research endeavor.

General comment: *The authors have the tendency to elaborate methods and techniques at irrelevant sections. Please, try to be more concise, it would help the reader to follow the manuscript.*

Reply to general comment: We accept the comment and revised the manuscript in several places following the specific comments.

Specific comments:

Comment 1: *L1 Why limit the presented method to groundwater protection? Also agriculture management could benefit from knowing the amount of leached nitrate. I suggest the following title: ‘Real-time monitoring of nitrate in soils.’*

Reply to comment 1: We agree with the comment and believe that the benefit to the agricultural sector is as important as protecting groundwater from pollution hazard. As such we take the reviewer advice and revised the title to include both the agricultural and environmental aspects. Accordingly, the new title is: “Real-time monitoring of nitrate in soils as a key for optimization of agricultural productivity and prevent groundwater pollution”.

Comment 2: *L 11 - 12 ‘Rising nitrate...’ – delete this sentence, you already mentioned the problems arising from overuse of nitrate.*

Reply to comment 2: It is truth that overuse of fertilizers in agriculture may end in down leaching of nitrate to groundwater (previous sentence). Nevertheless, the sentence “Rising nitrate concentration in aquifers is recognized as a worldwide environmental problem that contributes to water scarcity” give a hint to the severity of the phenomenon as a global threat to water resources in general, and particularly to groundwater. Therefore, although part of it is somewhat redundant to professional eyes, we believe that in this particular case elaboration is important even if it include a short repletion.

Comment 3: *L 12 I suggest ‘The development of...’ Line 22: delete ‘the’ and add ‘s’ to soils*

Reply to comment 3: Comment accepted, and the text was revised accordingly (line 13).

Comment 4: L 22 – 26: *'The system ...' delete. The abstract should be concise.*

Reply to comment 4:

The last two sentences of the abstract provide the reader with three very important aspects: (1) scientific-impact of irrigation pattern on nitrate mobility, (2) Agricultural yield - optimization of fertilizers application for improvement of field production, and (3) Water resources protection. Nevertheless, we agree with the reviewer that a concise abstract is essential, and we revised these sentences to improve clarity while keeping notion of the three aspects. "Real-time, high-resolution measurement on nitrate concentration in the soil revealed the complex variations in soil nitrate concentrations in response to fertigation pattern. Such data is crucial for optimizing fertilizer application and reduce the pollution potential of groundwater." (Line 25).

Comment 5: L 28 – 34 *I suggest to include two main challenges with nitrate fertilizer application. The first problem, as was mentioned in the referred lines, is the water resources pollution by nitrate. Note that the references related only to groundwater resources. You should indicate that there are other water resources, such as rivers, which are affected by nitrate. The other issue is agriculture management. For example, the method can help the farmer to time the nitrate fertilization application. You should indicate the challenges that agriculture management is facing with regards to nitrate application, just mention it concisely in a couple of lines. Delete the sentence regarding the Israeli problem, 'In Israel...'. You want to generalize your contribution.*

Reply to comment 5: We agree to the reviewer's comment that nitrate pollution is not only in concern to groundwater resources and the manuscript is revised to account for surface water (lines 29 - 31). Additionally, the section regarding nitrate pollution of groundwater in Israel has been deleted. Finally, the possible gain from nitrate monitoring in soils in regards to agriculture management and fertilizer application timing had been added to the manuscript (lines 44 - 46).

Comment 6: L 43 - 46: *I suggest moving these lines to the first paragraph.*

Reply to comment 6: Although both lines 51 - 54 and the first paragraph (lines 28 – 34) are dealing with groundwater pollution by nitrate, the first paragraph focuses mainly on the global problem of water pollution by nitrate, while lines 51 - 54 mainly attends on the limitation of the available technology to deal with real-time variability of nitrate in soils.

Comment 7: L 48 – 51 *I don't see the contribution of these lines to the introduction. You already mentioned the disadvantages in lack of real-time monitoring of nitrate. I suggest deleting these lines.*

Reply to comment 7: The comment is accepted, and the related text was deleted from the manuscript (lines 56 – 59).

Comment 8: L 52 *Today – delete*

Reply to comment 8: The comment is accepted, and the text was revised accordingly (line 57).

Comment 9: L 54 - 59 *'However, solution' I suggest deleting these lines. 'these methods are designed for water samples.' move to last paragraph, because the current manuscript describes the next step or evolution of these methods.*

Reply to comment 9: The comment is accepted, and the text was revised accordingly (line 59).

Comment 10: L 65 – 67 *delete. Put the references in line 65 after the words '...decades'.*

Reply to comment 10: The comment is accepted the manuscript was revised (lines 68 – 69).

Comment 11: L 67 – 98 I would move these lines to the method section. Here you talk about the challenges of applying the system at different environments. Or maybe make one paragraph, to explore the different implementations of the UV method.

Reply to comment 11: The manuscript in the mentioned lines is divided into three main sections. The first section (lines 71 - 80), brings a short description of past work showing the potential to use UV absorption spectroscopy to perform *in-situ* analyses of nitrate in soils. The second section (lines 81 - 88) shows a limitation which can occur when trying to apply UV absorption spectroscopy technique to measure nitrate in soil's porewater when Dissolved Organic Carbon (DOC) is present. The third section (lines 89 - 102) is a short review of studies that were trying to deal with the problem of measuring aqueous nitrate in the presence of DOC by few spectral techniques. At the course of this study we have tried, unsuccessfully to apply these methods for measuring nitrate in porewater samples from few agricultural sites, and with the presence of DOC. For this reason, this research was focusing on finding a robust method that would enable the use of UV absorption technique to monitor nitrate in soils, at high time resolution and with the presence of DOC. Therefore, the mentioned text (lines 71 – 102) is described as few case studies during the introduction section and not under the methodology section. We believe that this section improve clarity and essential as scientific background.

Comment 12: L 178 - 194 These are method descriptions. Please move these lines to the method section.

Reply to comment 12: The comment is accepted. A similar text appears in the methods section (lines 118 – 129) and therefore the current text has been removed from the manuscript.

Comment 13: L 196: ‘...between the two’ – which two, there are three wavelengths.

Reply to comment 13: The comment is accepted, and the text was clarified at lines 196 - 197.

Comment 14: L 226 – 228 This sentence is a bit vague. Do you want to say that the results indicate that different soil types should have different calibrations curves? Or in short, the soil texture might affect nitrate concentration readings using the UV method?

Reply to comment 14: The spectral analysis shows that different sites may have appropriate calibration curve for nitrate concentrations at different wavelengths, which implies the possibility of adopting a unique wavelength for each site. The manuscript was revised for clarified (lines 228 – 230).

Comment 15: L 230 – 236 These lines contain a mix of discussion and information, which makes it hard to follow. You can start this paragraph from ‘The absorption spectrum ...’ and delete the preceding lines.

Reply to comment 15: The reviewer comment is accepted, and the text was revised accordingly (line 232).

Comment 16: L 242 ‘it could be concluded’ - the conclusions section is at the end of the manuscript. Please rephrase the sentence.

Reply to comment 16: The comment is accepted, and the text was revised at line 238.

Comment 17: L 320 – 325 move these lines to the method section. Lines 339-342: ‘As ... equations’ delete these lines.

Reply to comment 17: Lines 319 - 324 are describing the last phase of an algorithm developed to overcome the difficulties of measuring nitrate in porewater samples containing DOC. Since the development of the algorithm is an outcome of this research, and it is not a standard analysis, it is brought under the results and discussion section rather than the materials and methods. Additionally, lines 338 – 343 (previously 339 – 342) had been revised to gain a more concise manuscript.

Comment 18: L 342 – 345 these lines should be in methods section.

Reply to comment 18: Lines 339 – 342 describes a test conducted to insure the previously described algorithm measurement accuracy and thus relevancy during long operations when the chemistry of the soil solution in the field may change in response to different seasonal events (temperature changes, different irrigation scheme, different crops, etc.). Since the understanding that variations in the solution chemical composition can lead to measurement drifts when applying UV absorption spectroscopy techniques, is one of the findings of this research, this chapter appears following the description of the newly developed algorithm at the results and discussion section.

Comment 19: L 346- 348: delete these lines. You mentioned the sampling dates earlier and if not do so.

Reply to comment 19: Comment is accepted. The manuscript of chapter “3.5. Stability and consistency of the specific calibration curves” been revised as elaborated under the replies for comments 18 and 20.

Comment 20: L 348 – 349 The sentence is vague, Do you mean that the August 2015 was used as a reference curve?

Reply to comment 20: The data collected from august 2015 samples were used as input for the site-specific algorithm, and as the algorithm output, a calibration equation at different wavelength were obtained for each field site. The stability of these calibration equations had been tested on samples from additional sampling campaigns later in 2015, and at 2017, where results from standard laboratory analyses (observed nitrate concentrations) were plotted in reference to the result of the calibration equation, obtained at august 2015 (predicate nitrate concentration).

To improve clarity the manuscript is revised (lines 343 - 348).

Comment 21: L 351 You use the word ‘accordingly’ far too many times. Delete ‘Accordingly’, and write ‘It suggests...’

Reply to comment 21: The comment is accepted, and text has been revised accordingly (line 348)

Comment 22: L 354 ‘be concluded’ - the conclusions section is at the end of the manuscript. Please rephrase the sentence

Reply to comment 22: The comment is accepted, and text has been revised accordingly (line 351)

Comment 23: L 359 - 371 Move to methods section

Reply to comment 23: A similar text appears in the methods section (lines 176 – 192) and therefore the current text has been removed from the manuscript.