

Dear Prof. Frans van Geer,

I enclose our revised manuscript entitled "Technical note: Field experiences using UV/VIS Sensors for high-resolution monitoring of nitrate in groundwater". We have amended the manuscript accordingly to the comments of the reviewers. We feel that the manuscript has been greatly improved by the comments and input from the reviewers.

Yours sincerely,

Manuela Huebsch

Reply to Dr. Rozemeijer (Referee #1)

We appreciate the constructive comments and suggestions from Dr. Rozemeijer. We have addressed the comments in our revised manuscript as described in the following.

Comments from Referee #1:

1) # 12293_8: Is 'breaching' common here? 'Exceeding' maybe better.

Response: We agree. We have replaced 'breaching' by 'exceeding'.

2) # 12293_9: Please add that this is the MAC for drinking water.

Response: We agree. We have added 'for drinking water'.

3) # 12293_21-23: Specify why these two sensors were tested. Are they the only systems using spectrophotometry available?

Response: The two sensors are not the only online UV/VIS spectrophotometers that are available on the market. For example, other sensors that are offered are Satlantic/ISUS V3 or YSI/NitraVis. However, the two sensors presented are often and widespread used for monitoring. Hach Lange GmbH is market leader in Europe. s::can Messtechnik GmbH has a worldwide network of more than 40 partners around the world.

4) # 12293_23: For comparison purposes, it seems more reasonable to apply both sensors at both locations. Please explain why one sensor was tested in Ireland and the other in Jordan.

Response: Primarily, the sensors were used for two independent studies which focused on different scientific research questions. A collaboration between the two research teams enabled to write a technical note about the UV/VIS sensors used. We have added 'which were originally used for two different scientific studies (Grimmeisen et al., 2014, Huebsch et al., 2014)'.

5) # Introduction: You may want to add info on what was already known about the performance of the sensors from the providers and from previous applications. And specify what you add to this existing knowledge.

Response: The authors have added the following information in the technical note: 'Some technical information about UV/VIS sensors in natural waters can be found in the literature (e.g. Drolc and Vrovsek, 2010; Thomas and Burgess, 2007; van den Broeke et al., 2006), but up to date there is no technical information available that describes a detailed comparison of widespread and commonly used online spectrophotometers and their positive and negative aspects. There is sparse information from the two manufacturers on sensor performance in natural waters.'

6) # 12296_14-16: Why does the manufacturer advise this?

Response: This comment relates to the following sentence: 'The manufacturer advises to use a path length of 35 mm in natural water, even if this might not be the optimal path length for the monitored NO₃-N concentrations in the field (optimal at ≤ 10 mg L⁻¹).' The reason is explained already in the following two sentences: 'If additional measuring options are included such as turbidity, TOC and DOC, the path length has to be suitable for the combined options. Those may occur at different ranges and the best compromise has to be selected.' We have added 'The reason is that' at the beginning of the two sentences to make it easier to understand for the reader.

7) # 12299_7-11: The setup was already described before.

Response: We agree. We have excluded the sentences 'Spring waters A and B were constantly monitored during the research period for the DWS and MWS, respectively. Spring water A was sampled in a karst spring in an agricultural dominated area in South Ireland, whereas spring water B occurs in an urbanized catchment and is continuously contaminated by faecal matter from sewer seepage of Salt, a city in Jordan.' We have changed the following sentence 'For Fig. 3, the spring water samples used have a similar NO₃-N concentration of 11.4 mg L⁻¹ and 11.1 mg L⁻¹, respectively' to 'Spring water sample A and B have a similar NO₃-N concentration of 11.4 mg L⁻¹ and 11.1 mg L⁻¹, respectively.' Furthermore, to provide the full information we have changed the following sentence in the Materials and methods section 'The DWS was installed in a flowing spring emergence (Spring A) in south-west Ireland and the MWS in a flowing spring emergence (Spring B) in Jordan.' to 'The DWS was installed in a flowing spring emergence (Spring A) in a karst spring in an agricultural dominated area in south-west Ireland and the MWS in a flowing spring emergence (Spring B) in an urbanized catchment in north-west Jordan.'

8) # 12299_14&16 and further: What is 'mains'?

Response: 'Mains water' is another word for 'tap water' or 'potable water' and is a widely used term.

9) # paragraph 3.3: Were the interfering substances not measured? What interfering substance caused the offset? Do you have info to quantify the interference by different substances?

Response: The offset of the spring-river-pond water in Fig. 3a) was demonstrated for illustration purposes to explain the principle of the sensor only. However, the offset was caused by increased absorption in the wavelength range between 250-400 nm which is an indicator for the presence of COD (van den broeke et al., 2006). The monitored water for research purposes was spring water A and B which was not or negligible influenced by interfering substances which can be also recognized in Fig. 2 (accuracy of the calibration). Thus, the authors did not measure interfering substances additionally. The manufacturers give no specification of problems with additional substances, but evidence can be find in the literature (e.g. Thomas et al. (1990), Kröckel et al. (2011), Langergraber et al. (2004)).

10) # 12300_19-20: consider rephrasing ‘calibration intervals can be performed on a long term basis’, eg: x month calibration intervals are sufficient’

Response: We have added ‘of up to two years’.

11) # 12300_26: precicion → precision

Response: Done.

12) # 12303_8: remove comma after although

Response: Done.

Reply to Referee #2

We appreciate the constructive comments and suggestions from Referee #2. We have addressed the comments in our revised manuscript as described in the following.

General comments from Referee #2:

1) I am missing some information on the statistics applied in the Method section and a description of the method applied in Fig. 3b.

Response: The complete statistics cannot be described as the full algorithm is kept as corporate secret by s::can Messtechnik GmbH and Hach-Lange GmbH. As the authors on the technical note are not involved with these companies, the focus in the technical note has been chosen on practical ‘field experiments’ as users of the sensors. However, the calculation for the first derivative can be included

in the technical note. We have added the following passage in the technical note: ‘In addition, the first derivative allows a finer interpretation of the nitrate content in the water. The first derivative can be determined as follows (Eq. 2 and Eq. 3):’

$$y'_n = \frac{y_{n+1}-y_n}{x_{n+1}-x_n}, \quad (2)$$

$$x'_n = \frac{x_{n+1}+x_n}{2}, \quad (3)$$

2) The authors should give an advice on how often you will need to take conventional water samples for nitrate analysis as mentioned on page 12300, line 28.

Response: The authors advise to take water samples every 3 to 6 months. We have added ‘in a time frame of 3 to 6 months’.

3) The way the sensor is installed in the water column is somewhat confusing as you mention both vertical and horizontal installations. It might be good to have a drawing of this installation principle together with Fig. 1.

Response: We have amended Figure 1 as suggested by the reviewer. The installation principle of the horizontal installation is now illustrated. We have chosen only to illustrate the horizontal installation principle as the vertical installation principle cannot be recommended. The authors feel that by illustrating the horizontal position the vertical position is self-explaining. We have also added ‘c) Principle of horizontal installation of the sensors’ in the legend.

Specific comments from Referee #2:

4) # Page 12294, line 18-20: This sentence should be elaborated a little more by the authors as the reader do not have a chance to understand the use of the two methods mentioned without having to read the cited literature.

Response: The comment refers to the sentence ‘The consequences are that multivariate data analysis approaches are needed to determine NO₃-N, such as principal component analysis or partial least square regression (Dahlén et al., 2000; Gallot and Thomas, 1993a; Karlsson et al., 1995; Macintosh et al., 2011). We have added the following passage: ‘The statistical approaches take the variances of the raw and observed dataset of absorbance values into account. Principal component analysis uses orthogonal transformation. Partial least squares analysis is based on determining the lowest variance of a linear regression line.’

5) # Page 12296, line 12: It seems strange to use a sensor that has a range lower than the one measured in the spring as 12-15 mg NO₃ on the page before? An explanation is given later under the results but should be given maybe better in this section.

Response: This comment is similar to comment 6 of Referee #1 and relates to the following sentence: ‘The manufacturer advises to use a path length of 35 mm in natural water, even if this might not be the optimal path length for the monitored NO₃-N concentrations in the field (optimal at ≤10 mg L⁻¹).’ The reason is explained already in the following two sentences: ‘If additional measuring options are included such as turbidity, TOC and DOC, the path length has to be suitable for the combined options. Those may occur at different ranges and the best compromise has to be selected.’ We have added ‘The reason is that’ at the beginning of the two sentences to make it easier to understand for the reader. In addition and in relation to comment 6) we have added more information as described in the next comment.

6) # Page 12296, line 27-28: The authors need to elaborate and give a little more details on these two functions for calibration for the readers to understand what is e.g. normally used.

Response: We have added the following sentence: ‘For both sensors the calibration that is normally chosen is based on a linear function. Calibration based on a polynomial function can lead to higher accuracy if a path length needs to be chosen that on the one hand represents a suboptimal path length for nitrate, but on the other hand offers the possibility to measure additional parameters.’

7) # Page 12297, line 12: Please give information on the name and number of the advanced and comparable versions used for costing.

Response: The information is already included in the Materials and methods section: ‘In this study, a DWS (NITRATAX plus sc, Hach Lange GmbH, Germany) and a MWS (s::can spectro::lyser™, s::can Messtechnik GmbH, Austria) were used’. As the authors feel that this information is only a repetition, we did not include this information twice.

8) # Page 12297, line 20-22: This sentence seems to explain Fig. 2 but suddenly Fig. 3a is also referred – please clarify this as it is not obvious for the reader.

Response: The authors agree that the information is not necessary at this point. Thus, we have kept ‘(spring water A;’ and excluded ‘Fig. 3a)’.

9) # Page 12298, line 24: Please clarify what is meant by the word “trueness”.

Response: The authors feel that the sentence can be modified to ‘Complex changes of the water matrix can affect the precision of the sensor readings,...’.

10) # Page 12299, line 9-11: This sentence seems to be a repetition from the Materials and Method section so please avoid here.

Response: We agree. As also stated to Referee #1, we have excluded the sentences ‘Spring waters A and B were constantly monitored during the research period for the DWS and MWS, respectively. Spring water A was sampled in a karst spring in an agricultural dominated area in South Ireland, whereas spring water B occurs in an urbanized catchment and is continuously contaminated by faecal matter from sewer seepage of Salt, a city in Jordan.’ We have changed the following sentence ‘For Fig. 3, the spring water samples used have a similar NO₃-N concentration of 11.4 mg L⁻¹ and 11.1 mg L⁻¹, respectively’ to ‘Spring water sample A and B have a similar NO₃-N concentration of 11.4 mg L⁻¹ and 11.1 mg L⁻¹, respectively.’ Furthermore, to provide the full information we have changed the following sentence in the Materials and methods section ‘The DWS was installed in a flowing spring emergence (Spring A) in south-west Ireland and the MWS in a flowing spring emergence (Spring B) in Jordan.’ to ‘The DWS was installed in a flowing spring emergence (Spring A) in a karst spring in an agricultural dominated area in south-west Ireland and the MWS in a flowing spring emergence (Spring B) in an urbanized catchment in north-west Jordan.’

11) # Page 12299, line 11-20: These sentences referring to Fig. 3 is not really clear for the reader – why these four types are used and they seems to be used for both types of sensors even though taken in respectively, Jordan and Ireland?

Response: In Fig. 3 absorbance vs. wavelength of four different water samples is illustrated to describe the general working principle of the sensors for the reader. Those water samples were not used for both types of the sensors. In the technical note, an additional passage has been added to clarify this to the reader: ‘Fig. 3 shows absorbance spectra and first derivative of four different water samples, which were determined with the MWS, to illustrate the general working principle of UV/VIS monitoring.’

12) # Page 12299, line 20: What is meant with Isobestic – please explain more about this for the reader.

Response: The authors have modified the following sentence to clarify ‘isobestic’ for the reader ‘Isobestic points are an indicator for different matrix compositions of the samples (Gallot and Thomas, 1993b; Vaillant et al., 2002).’ To ‘Isobestic points, that describe the wavelength at which two absorbance spectra are crossing, are an indicator for different matrix compositions of the samples (Gallot and Thomas, 1993b; Vaillant et al., 2002).

13) # Page 12300, line 1: The first derivative should be explained in the Materials and Method section and also in the Fig. 3b on the y-axis text.

Response: The authors know that the first derivative plays an important role in the determination of the nitrate values for the MWS due to personal communication with the company. Nevertheless, the exact algorithm is not known as this is kept as corporate secret by the company. The y-axis of the first derivative is mathematically defined as y' or $f'(x)$. In this case it is Absorbance'. Absorbance' has been added to the axis in the diagram.

14) # Figure 2: The equation in Fig 2a cannot be right as the slope is > 1 and the line is under 1:1 line. Also the legend text should be improved and be more easy to read as it is very long and difficult to follow – what is meant by error bars were calculated after the manufacturers specifications? Please give details on statistics in the Materials and Methods section.

Response: Thank you for this comment. The correct equation in Fig. 2a has been added ($y = 0.51 + 0.91x$). We have shortened the legend by the following sentences 'To test the accuracy of the DWS, while considering the matrix composition of the studied water, spring water (highest concentration), water from a close-by river (lowest concentration) and a mix of river and spring water was used. For the MWS, spring water and water from other close springs were used. Error bars were calculated after the manufacturers specifications.' Those sentences were added in 3.2. Ease of calibration and accuracy after calibration without the sentence 'Error bars were calculated after the manufacturers specifications.' which is described in more detail as follows.

The manufacturer gives detailed information of the expected error bar interval. For the DWS the error bar interval is calculated by the following equation: concentration error bar interval = $0.03 * \text{measured concentration} + 0.5$. For the MWS the error bar interval it is: concentration error bar interval = $0.02 * \text{measured concentration} + 1/\text{path length of the sensor}$. In our case the path length is 35. We have added this information in the section of the description of Figure 2: 'The error bars were determined by the manufacturers specification of the expected concentration interval which is 'concentration error bar interval = $0.03 * \text{measured concentration} + 0.5$ ' for the DWS and 'concentration error bar interval = $0.02 * \text{measured concentration} + 1/\text{path length of the sensor}$ '.'

15) # Figure 3: Also here the legend text is difficult to understand (e.g. isobestic) for the reader and please define the y-axis in Fig 3b.

Response: We have added 'that describe the wavelength at which two absorbance spectra are crossing' to isobestic points in the legend for better understanding. The y-axis has been defined in the figure as requested in 13) and 15).