Technical note: Field experiences using UV/VIS Sensors for high-resolution monitoring of nitrate in groundwater

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Abstract:

Two different in-situ spectrophotometers are compared that were used in the field to determine nitrate-nitrogen (NO_3-N) concentrations at two distinct spring discharge sites. One sensor was a double wavelength spectrophotometer (DWS) and the other a multiple wavelength spectrophotometer (MWS). The objective of the study was to review the hardware options, determine ease of calibration, accuracy, influence of additional substances and to assess positive and negative aspects of the two sensors as well as troubleshooting and trade-offs. Both sensors are sufficient to monitor highly time-resolved NO_3-N concentrations in emergent groundwater. However, the chosen path length of the sensors had a significant influence on the sensitivity and the range of detectable NO_3-N. The accuracy of the calculated NO_3-N concentrations of the sensors can be affected, if the content of additional substances such as turbidity, organic matter, nitrite or hydrogen carbonate significantly varies after the sensors have been calibrated to a particular water matrix. The MWS offers more possibilities for calibration and error detection, but requires more expertise compared with the DWS.

1. Introduction

Present and predicted future shortage of drinking water is a worldwide problem and global population growth increases the demand for high-quality potable water (Schiermeier, 2014). Thus, the importance of the protection of drinking water quality is acknowledged worldwide by the implementation of international programs such as the European Union (EU) Water Framework Directive (OJEC, 2000) and daughter directives, the US National Water Quality Assessment Program (NAWQA) and Maximum Daily Load Program (TMDL) (Elshorbagy et al., 2005) or the Australian National Water Quality Management Strategy (ANZECC, 2000). Built into these regulations is a fundamental need to monitor the quality of drinking water supplies. However, especially in karst and/or fractured aquifers, water quality can change rapidly in a time frame from hours to days (Huebsch et al., 2014; Mahler et al., 2008; Pronk et al., 2009). Nitrate (NO_3^-) is particularly noted as being a risk to human health when in high concentrations in source drinking water (L'hirondel, 2002) and also contributes significantly to eutrophication of water (Stark and Richards, 2008).

High resolution flow and nitrate-nitrogen (NO_3-N) concentration data from short residence time aquifers enable an improved understanding of the mobilisation/dilution dynamics in karst aquifers (Huebsch et al., 2014) and to prevent negative consequences from NO_3-N concentrations exceeding the maximum allowable concentration (MAC) for drinking water. In the EU for example, the MAC is 11.3 mg NO_3-N L^{-1}, to prevent health concerns (Knobeloch et al., 2000), abortion to cattle or toxicity in livestock (Di and Cameron, 2002).

Photometrical ultraviolet/visible light (UV/VIS) sensors have been first employed at municipal wastewater treatment plants to control NO_3-N effluent concentrations (Langergraber et al., 2003; Rieger et al., 2004). In addition, UV/VIS sensors have been recently used in groundwater and surface water applications to assess highly resolved NO_3-N concentrations (Pu et al., 2011; Wade et al., 2012). The technique gives the opportunity to observe trends and rapid changes of NO_3-N whilst using a solid-state methodology without reagents. Thus, less frequent calibration and maintenance than other common in-situ methods such as ion sensitive electrode applications is required (Bende-Michl and Hairsine, 2010). 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.

The technical note provides an assessment of two different spectrophotometric sensors, i.e. a double wavelength spectrophotometer (DWS) and a multiple wavelength spectrophotometer (MWS) used at field sites in Ireland and Jordan, respectively, which were originally used for two different scientific studies (Grimmeisen et al., 2014; Huebsch et al., 2014). The following issues are addressed in the present study: Hardware options, ease of calibration, accuracy, influence of additional substances, positive and negative aspects of the two sensors, troubleshooting and trade-offs.

2. Materials and methods

NO_3-N dissolved in water absorbs light below 250 nm (Armstrong, 1963) although the specification for NO_3-N determination due to absorbance varies in the literature. Karlsson et al. (1995) and Drolc and Vrtovšek (2010) describe specific parameter determination of NO_3-N at 205 nm, Thomas et al. (1990) at 205 to 210 nm, Ferree and Shannon (2001) at ~224 nm and Armstrong (1963) at 227 nm. The relationship between absorbance, i.e. extinction of light (E) at a specific wavelength, and NO_3-N concentration is linear and follows the Lambert Beer´s Law (Eq. 1):

$$E = log\frac{I_0}{I}, \qquad (1)$$

where I_0 is the light intensity emitted by the sensor lamp and I is the light intensity after the light has passed the water matrix. Hence, physically increased light absorption of NO_3-N dissolved in water correlates to increased NO_3-N concentrations. However, in natural water, additional substances other than NO_3-N occur. Turbidity has a major influence on light absorbance as the presence of suspended material such as organic particles can lead to scattering effects on the recorded absorption values of NO_3-N (Chýlek, 1977; Rieger et al., 2008; Vaillant et al., 2002). In addition, substances that absorb in the investigated spectral range such as nitrite-nitrogen (NO_2-N) or humic acids can lead to superposition of absorbance (Kröckel et al., 2011). The consequences are that multivariate data analysis approaches are needed to determine NO_3-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). 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. 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):

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

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

In this study, a DWS (NITRATAX plus sc, Hach Lange GmbH, Germany) and a MWS (s::can spectro::lyser^{TM}, s::can Messtechnik GmbH, Austria) were used (Fig. 1). 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. The study sites are described in more detail in a previous study of Huebsch et al. (2014) and Grimmeisen et al. (2014), respectively. Both springs discharge karst aquifers; however, Spring A is located in an agricultural catchment and Spring B in an urban catchment.

The DWS measures UV absorbance at a wavelength of 218 nm at a measuring receiver (EM – element for measuring) and at 228 nm at a reference receiver (ER – element for reference). The recorded measurements at two different wavelengths at EM and ER are designed to compensate interference of organic and/or suspended matter (Thomas et al., 1990) by interpreting the difference between the absorbance values at EM and ER which is expressed by ΔE. In comparison, a UV sensor using only one single wavelength is not able to compensate additional interferences (van den Broeke et al., 2006). The MWS measures absorbance at 256 different wavelengths between 200 nm and 750 nm within 15 sec (Rieger et al., 2004). Both sensors feature the possibility to export the monitored absorbance values and the calculated concentrations. As a result of the different measuring methods, the DWS makes no difference between NO_3-N and NO_2-N and therefore, reports the NO_x-N concentration (or total oxidised nitrogen, TON) instead of NO_3-N (Drolc and Vrtovšek, 2010) and assumes negligible NO_2-N. Due to the range of measurements in the scan, the MWS is able to provide the specific NO_3-N concentration. NO_3-N/NO_x-N concentrations observed with the DWS and MWS were compared with NO_3-N/NO_x-N concentrations determined in the laboratory. Water samples used for determination of NO_3-N/NO_x-N concentrations were measured in the water in situ with the sensors. For comparison, water samples were also filtered using a 0.45 -µm micropore membrane to determine NO_3-N/NO_x-N concentrations in the laboratory. For determination Aquakem 600A (Thermo Scientific, Finland) and Dionex ICS-2100 (Thermo Scientific, Finland) was used, respectively. The DWS was installed in July 2011 in spring A. NO_x-N concentrations were fluctuating approx. between 10 mg L^{-1} and 14 mg L^{-1} until September 2014. The MWS was installed in spring B in May 2011 and observed approx. minimum and maximum concentrations of 11 mg NO_3-N L^{-1} and 15 mg NO_3-N L^{-1} until September 2014, respectively.

There are several sensor options available for the DWS and the MWS from the manufacturers. The DWS is available with three different path-lengths of 1, 2 and 5 mm, which cover a NO_x^-N detection range of 0.1 to 100.0 mg L^{-1}, 0.1 to 50.0 mg L^{-1} and 0.1 to 25.0 mg L^{-1}, respectively. The range of NO_x^-N detection increases with a shorter path length. However, a shorter path length implies also a lowered overall sensitivity of the measurement (Thomas et al., 1990). In this study, a DWS with a path length of 5 mm was used.

There are also several options for the MWS for possible measuring paths and applications. For natural waters, it is advisable to choose a measuring path of 5, 15 or 35 mm. A measuring path of 5 mm covers a NO_3-N detection range of 0.02 to 70.0 mg L^{-1}, a measuring path of 15 mm a detection range of 0.02 to 40.0 mg L^{-1} and a measuring path of 35 mm a detection range of 0.02 to 10.0 mg L^{-1}. Thus, the advised measuring paths for both sensors differ by the manufacturers due to the divergent measuring methods. The studied MWS had a measuring path of 35 mm and the software capability to measure turbidity, NO_3-N, total organic carbon (TOC) and dissolved organic carbon (DOC). 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 NO_3-N concentrations in the field (optimal at $\leq$10 mg L^{-1}). The reason is that 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.

For calibration, the applied DWS has the option for a two-point calibration, in addition to a four-point manufacturer´s calibration with standard solutions at 0, 25, 50 and 100 mg L^{-1}. The MWS offers two main options for calibration, off-site and on-site calibration, which are also in addition to the manufacturer pre-adjustment. The off-site calibration is based on wavelength-concentration datasets previously analysed by the manufacturer (Langergraber et al., 2004c), whereas the on-site calibration offers the possibility for an improved adaption to the matrix of the monitored water (Rieger et al., 2006). This is also possible with the DWS. On-site calibration can be performed with a linear (local 1) or a polynomial (local 2) function. 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.

3. Results and discussion

3.1 Hardware options

Table 1 provides an overview of the available hardware and software options, output format, maintenance, warranty and costs of the DWS and MWS. Important differences between both sensors despite the measuring method are: 1) the cleaning device for the MWS is offered as an additional hardware option, (but highly necessary in natural waters,), whereas the DWS is already equipped with a wiper for cleaning; 2) the purchase price for the DWS is lower than the MWS (~16.000 € and 20.000 € excluding VAT in 2014, respectively). Both sensors report the raw dataset of the absorbance measurements, which is based on the two different measuring methods (DWS: two wavelengths; MWS: full absorbance spectrum). The investment costs for both sensors are based on the advanced and comparable version of both manufacturers, which means that first, turbidity can be compensated, second, the raw dataset is included and third, error detection for both sensors is possible afterwards. The costs are based on elementary equipment: sensor, cable and basic handling device. Additional upgrades such as remote control, advanced handling device and flow-through unit, which ensures sufficient flow through the measuring slit, are also available which lead to an increase in pricing.

3.2 Ease of calibration and accuracy after calibration

Fig. 2 shows the accuracy of the two sensors immediately after calibration using the available calibration methods. The error bars were determined by the manufacturers specification of the expected concentration interval which is ‘concentration error bar interval = 0.03 * measured concentration + 0.5’ for the DWS and ′concentration error bar interval = 0.02 * measured concentration + 1/path length of the sensor’. The DWS was calibrated with standard solutions, which provided a good result for the monitored water in the area (spring water A). To test the accuracy of the DWS, while considering the matrix compostion 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 testing the accuracy of the MWS, spring water and water from other close springs were used. The root mean square error (RMSE) to the ideal straight line of y = x (measured sensor concentrations vs. concentrations measured in the laboratory) was 0.42. For the MWS, higher accuracy was reached by using water samples from adjacent springs, which had a higher affinity to the water matrix of the monitored spring than standard solutions (spring water B; Fig. 3b). These water samples were also used to test the accuracy of the sensor. The best results were obtained with the on-site calibration using a second order polynomial function (local 2; Fig 2d) including a RMSE of 0.36. For off-site calibration (Fig 2b) and on-site calibration with a linear function (local 1; Fig. 2c) RMSE was 2.11 and 0.82, respectively. In addition, Fig. 2 shows that the accuracy of the sensor decreases with higher NO_3-N concentrations, especially for the two point calibration of the DWS sensor and the off-site calibration of the MWS. In general, the precision of the sensor readings are dependent on the sensor path length (Kröckel et al., 2011). The MWS with 35 mm path length becomes less accurate with higher concentrations, as the optimal measurement range for 35 mm path length is 0.02 to 10 mg L^{-1} NO_3-N. However, the manufacturer claims the NO_3-N concentration range between 10 to 15 mg L^{-1} to be sufficient and applicable for monitoring. The path length of 35 mm was recommended for including additional measuring options such as turbidity, TOC and DOC. The accuracy of both sensors is dependent on a) the selected path length for measuring the concentrations, b) a comparable and similar water matrix to the standard solution used for calibration and/or c) the option to use local water having minimum and maximum NO_3-N concentrations characteristic for the NO_3-N measured with similar matrix structure for calibration. As the last two points are rather challenging in the field, we suggest calibrating the sensors with water from the field site. If necessary a number of those waters can be used that are diluted or concentrated with standard solution to get approximate representative minimum and maximum values for calibration. However, after calibration changes of the water matrix in a natural environment due to e.g. mixing of different groundwater can lead to less qualitative results. Complex changes of the water matrix can affect the precision of the sensor readings, because the sensor is calibrated to a specific water composition (Langergraber et al., 2004b; Maribas et al., 2008; Stumwöhrer et al., 2003).

3.3 Influence of additional substances

In natural waters, the absorption spectra can vary significantly due to, for example, different contents of natural organic matter (Thomas and Burgess, 2007) and so interference effects of substances that are absorbing light in a similar wavelength range to NO_3-N are possible (Macintosh et al., 2011). 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. Spring water samples A and B have a similar NO_3-N concentration of 11.4 mg L^{-1} and 11.1 mg L^{-1}, respectively. For comparison, two other samples with similar NO_3-N concentrations of 3.9 and 4.1 mg L^{-1}, respectively, were plotted: a sample of mains water of the Jordanian city, a water mix of spring, river and pond water sampled and mixed at the area in South Ireland mentioned above. The mains water is a mix of treated spring and river water, whereas the spring-river-pond water is a mix of water from spring water A, a nearby river and water from a pond. In Fig. 3a, the high absorbance values below 250 nm specify the presence of NO_3-N in the water. 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). Other substances such as NO_2-N, HCO_3^- or dissolved organic matter in water can result in a superposition of the absorbance values (Kröckel et al., 2011; Langergraber et al., 2004a; van den Broeke et al., 2006), even if the maximum absorbance values of those substances occur at different wavelengths than NO_3-N absorbance. In Fig. 3, the water mix of spring, river and pond water has higher absorbance values than the other samples, although the NO_3-N content is low in relation to spring waters A and B. This can be explained by the influence of interfering substances other than NO_3-N, which are leading to superposition of the absorbance values and are clearly indicated by increased absorbance values above 250 nm. The first derivative allows a more detailed interpretation of the NO_3-N concentration: Samples with similar NO_3-N concentration follow a much more similar curve progression (Fig. 3b) than the absorbance spectra (Fig. 3a). In addition, positive values in the majority of the first derivative between 220 and 240 nm indicate that the light or energy source is damaged and needs to be replaced. The MWS uses derivative methods, amongst others, for calculating the NO_3-N concentrations, whereas the DWS records the absorbance values at two wavelengths (218 and 228 nm) and defines the NO_x-N concentration by using the difference between those wavelengths. This means that the DWS sensor takes the slope into account as well as the interval of the absorbance difference at the two wavelengths, which implies that superposition by additional substances are considered. Nevertheless, this and other studies indicate problems due to superposition of substances (Maribas et al., 2008).

3.4 Positive and negative aspects of the two sensors

Table 2 gives an overview of positive and negative aspects of the two sensors regarding installation, requirements, calibration and error detection. Installation of both sensors is straightforward. The manufacturer of the DWS supplies L-brackets for installation of the instrument in the correct position. For both sensors, a mains power source is required for operation, which may be a problem for field applications. A power supply of 230vAC is sufficient. Positive aspects of both sensors are that the calibration intervals can be performed on a long term basis which is an asset compared to other NO_3-N detection methods (Beaupré, 2010). Calibration can be simple, if the water matrix is similar to standard solutions provided by the manufacturer, but more complicated if the water matrix differs significantly from standard solutions or if collection of water samples representing a broad range of NO_3-N concentrations of the monitored water is difficult. The MWS offers more options for calibration than the DWS, which can lead to higher precision (Fig. 2). In contrast, the on-site calibration methods require more expertise and, therefore, can be time consuming. Even if calibration intervals are on a long-term basis of up to two years, it is advisable to perform regular controls in a time frame of 3 to 6 months such as regular conventional measurements of NO_3-N concentrations to ensure the reliability of the data provided by the sensor. In addition, the manufacturer of the DWS advises to return the sensor to the manufacturer on an annual basis to refresh the four-point calibration, replace seals and check the sensor. Error detection is possible with both sensors, but costs more compared to similar sensor types provided by the manufacturers with no error detection. The manufacturer gives advice to check the light source every two years as this has to be renewed. Because the MWS measures the full absorption range, more detailed information of possible disturbances can be utilised.

3.5 Troubleshooting and trade-offs

During operation of both sensors, two difficulties occurred that affected the reliability of the recorded NO_x-N concentrations (Fig. 4, Fig. 5). Fig. 4 illustrates discrepancies between wavelength measurements and calculated NO_x-N concentrations above 12.12 mg L^{-1} of the DWS. In Fig. 4a, the raw dataset of the difference between absorbance values at 218 and 228 nm, ΔE, is shown. In Fig 4b, the reported NO_x-N concentrations are illustrated, which were calculated from the raw dataset and followed an inverse trend if NO_x-N concentrations were above 12.12 mg L^{-1}, contrary to Lambert Beer's Law. The manufacturer assumed a software problem and the probe had a complete control check after the detection of the error. The manufacturer's background calibration was therefore refreshed and the software and light source were replaced. However, because the raw absorption dataset was recorded, it was possible to eliminate the error retrospectively and quantitatively by using a regression line, which was extrapolated from the correct calculated values (Fig. 4c).

During operation of the MWS, suspicious readings were recorded, which occurred immediately after installation due to a technical mistake (Fig. 5). The sensor was first installed in a vertical position without a cleaning device. This led to an accumulation of suspended material at the measuring slit. Consequently, the recorded values for turbidity increased. If the turbidity signal reaches values at or above 20 FTU (Formazin Turbidity Units), determined NO_3-N values are not reliable. For turbidity $\geq$ 20 FTU the recorded NO_3-N values showed a decreasing trend. At turbidity $\geq$ 80 FTU no NO_3-N concentrations were reported. The sensor was cleaned on a weekly basis, which explains the periodic, weekly pattern of turbidity and NO_3-N values. After error detection, the sensor was reinstalled in a horizontal position with a downwards orientated measuring path. However, it was necessary to purchase a cleaning device from the manufacturer as fouling of the measuring slit still disturbed the readings. The manufacturer offers the sensor with the purchase of an air pressure cleaning device as an option (Tab. 1). In contrast, the DWS uses a wiper for cleaning, which is already included in the standard probe. Hence, we strongly recommend purchasing the cleaning device together with the MWS sensor, if the system is operated in natural waters.

During operation of the DWS the computer system was unstable and shut down several times causing data gaps of several hours, until the system started recording again. Maribas et al. (2008) also describes disturbances of the MWS measurements caused by air bubbles in the water. They state that where bubbles exist in the water, the measuring path needs to be orientated to allow the bubbles to pass. Kröckel et al. (2011) advises to use a filter such as a flow through-unit to prevent inaccurate measurements due to air bubbles (Tab. 1) although these can be unreliable in highly turbid waters. One should also notice that reliable measurements of both sensors cannot be determined, if the sensor measurements are affected by saline water. If the measured water is influenced by water with salt content, for example due to flooding and close installation to the coast or in deeper wells, the determination of NO_3-N by the UV sensors would be affected as salt has a strong UV absorption in the NO_3-N absorption range (Kröckel et al., 2011). In addition, in highly heterogeneous environments, such as karst aquifers, rapid groundwater fluctuations and temporary activated conduit inlets might result in mixing of waters with different water quality and therefore matrix. This can have an effect on the accuracy of the NO_3-N concentration dataset. Even though the MWS measures over the full absorption spectra, detections remain difficult in that case and might result in less accurate concentrations. This could be a problem especially if absolute values instead of general water quality trends are necessary in a rapidly changing environment. However, both sensors offer a reliable detection of highly resolved NO_x-N concentration trends with low maintenance effort, which is an asset in the field compared to other common in-situ methods such as ion sensitive electrode applications (Bende-Michl and Hairsine, 2010).

5. Conclusions

Both sensors were efficient for continuously monitoring highly time-resolved NO_3-N in groundwater emergences (i.e. flowing water) in this study and deemed fit for purpose. Although the calibration procedure for the DWS is easier than for the MWS, the wavelength spectra of the latter provides a more detailed insight of the absorption and consequently improved NO_3-N calculations. If NO_2-N is a major concern in the studied water, the MWS should be chosen for monitoring, as the DWS does not distinguish between NO_3-N and NO_2-N. For ease of use and with an emphasis on measuring TON (where NO_2-N is known to be negligible), the DWS could be also considered. In addition, the path length of the two sensors should be carefully chosen. The chosen path length is significant for the accuracy of the sensor measurements at a specific measurement range. It is reasonable to conclude that high-resolution UV/VIS monitoring will greatly contribute to a better understanding of groundwater processes in the future.

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Figures

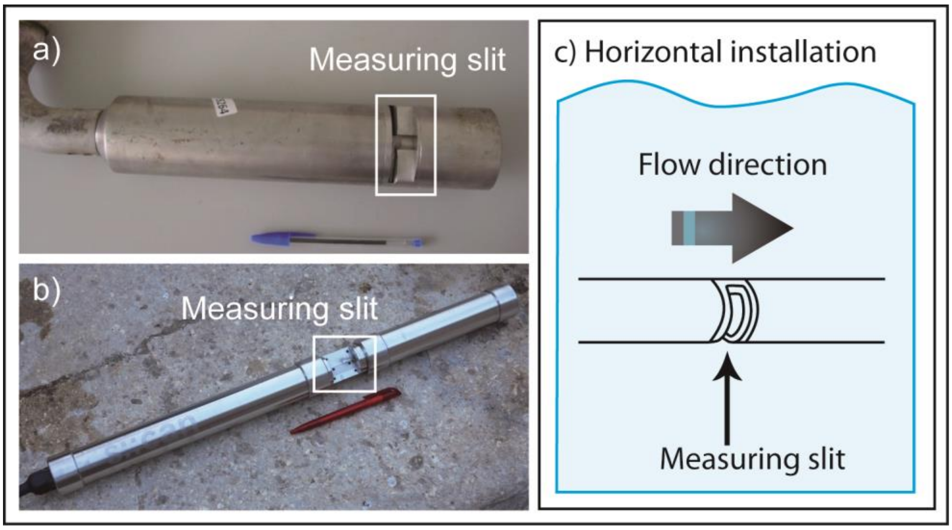

Figure 1: UV/VIS sensors: a) Double wavelength spectrophotometer (DWS) with measuring path of 5 mm; b) Multiple wavelength spectrophotometer (MWS) with measuring path of 35 mm; c) Principle of horizontal installation of the sensors.

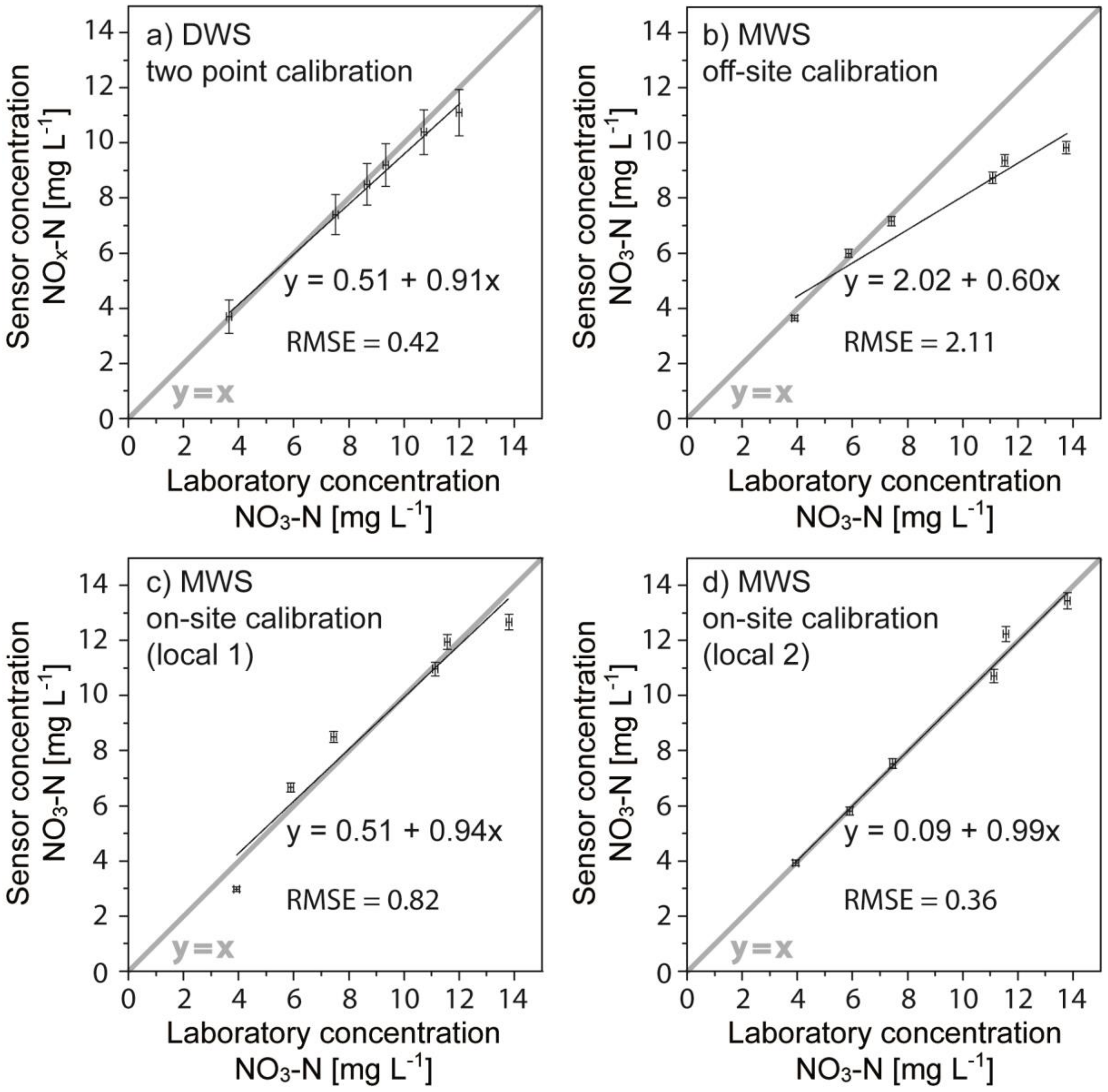

Figure 2: Accuracy of double wavelength spectrophotometer (DWS) and multiple wavelength spectrophotometer (MWS) immediately after calibration. Recorded sensor measurements are compared with measured concentrations analysed in the laboratory. The root mean square error (RMSE) was calculated by relating the measured sensor concentrations with the optimum calibration (ideal straight line y = x).The DWS has one option for calibration, whereas the MWS offers three options for calibration. All calibration options are in addition to the factory calibration provided by the manufacturer.

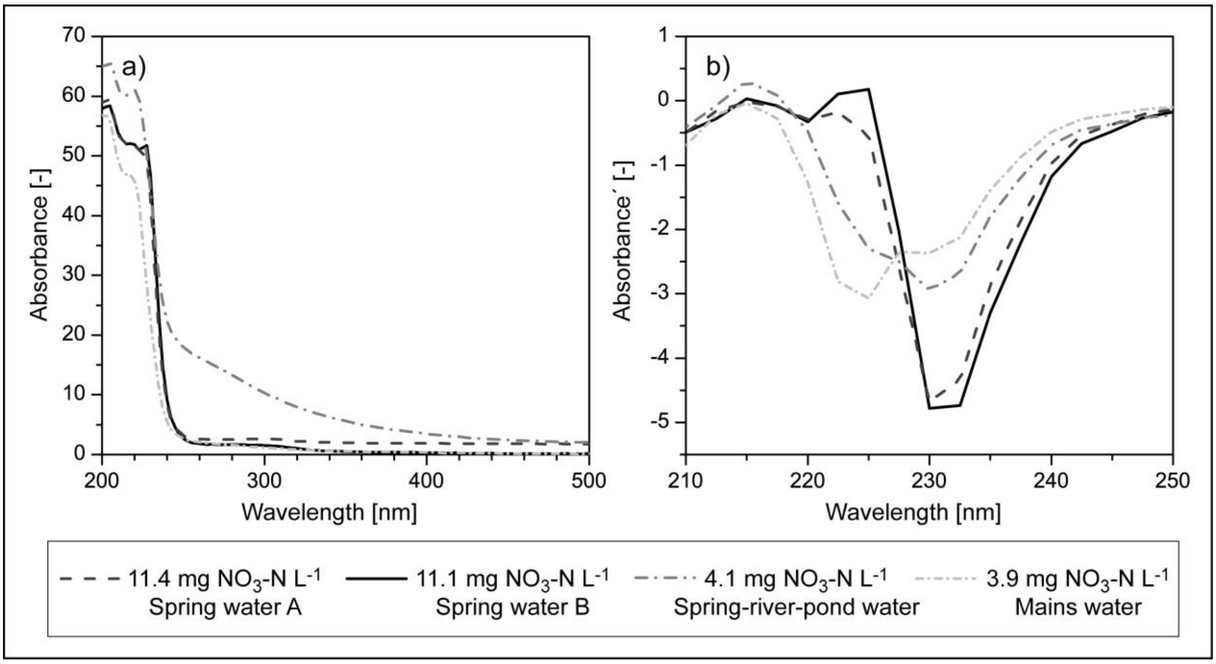

Figure 3: Absorbance vs. wavelength of 4 different samples measured with the multiple wavelength spectrophotometer (MWS). Spring water A was constantly monitored by the double wavelength spectrophotometer (DWS), whereas spring water B was the monitored by MWS. a) The isobestic points, that describe the wavelength at which two absorbance spectra are crossing, indicate different matrix compositions of the samples. Nitrate and nitrite are strongly absorbed below 250 nm. Other substances such as of COD (chemical oxygen demand), trace organics, humic substances or turbidity in water can increase the absorbance value below 250 nm. The maximum influence of those substances can be recognised at higher wavelengths, for example at the obvious differences of the samples between 250 and 400 nm. b) The first derivative of samples allows a finer interpretation of the nitrate content in the water. The samples with similar nitrate concentration show more similar curve progression than in a).

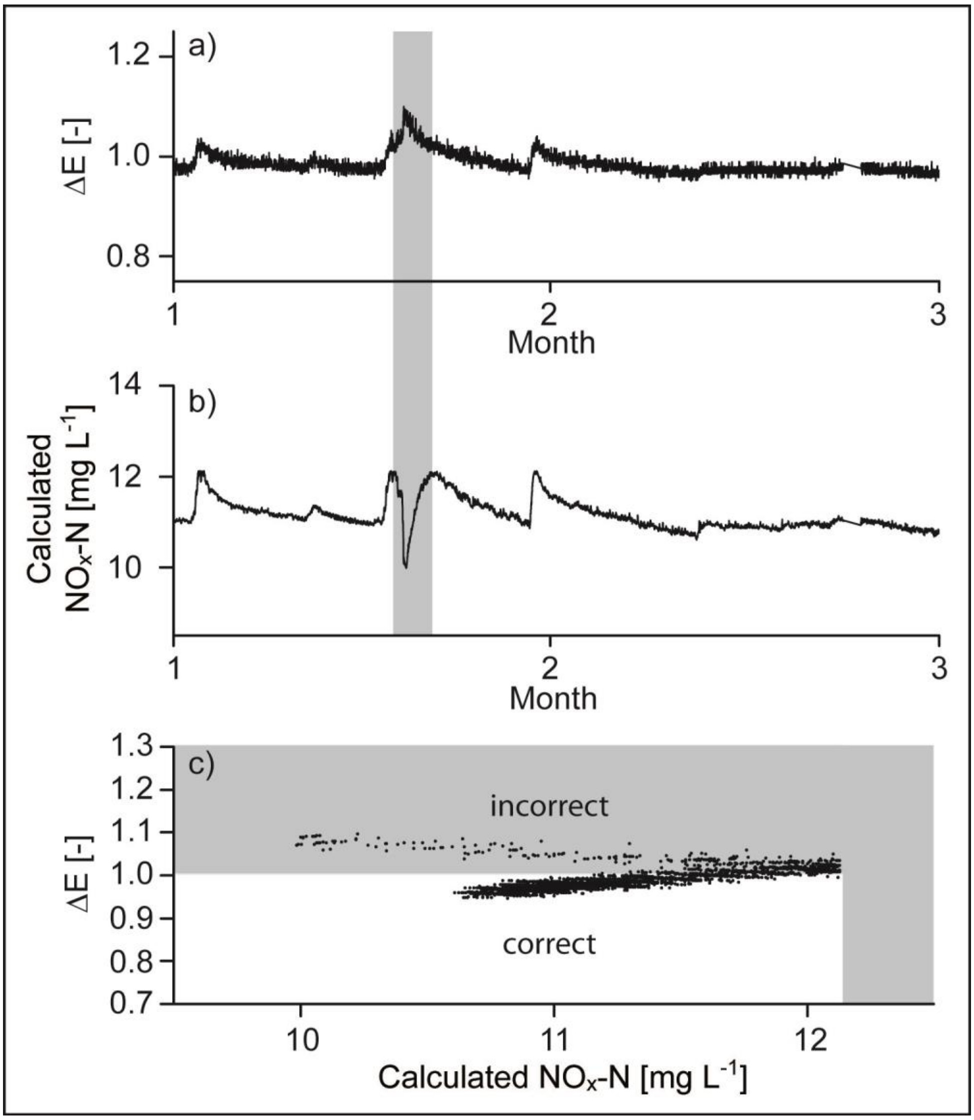

Fig. 4: Example of discrepancies between wavelength and calculated NO_x-N concentrations as displayed by the double wavelength spectrophotometer (DWS). The shaded grey area highlights the dataset of incorrect NO_x-N calculated values. a) Raw dataset of recorded wavelength values during 2 months. ΔE is the difference between light extinction at 218 and 228 nm. b) Calculated NO_x-N concentrations from the raw dataset as reported by the DWS. c) Values of the raw dataset (ΔE) and the reported NO_x-N concentrations of the DWS. Once NO_x-N values reached 12.12 mg L^{-1}, values were incorrectly calculated in an opposite trend.

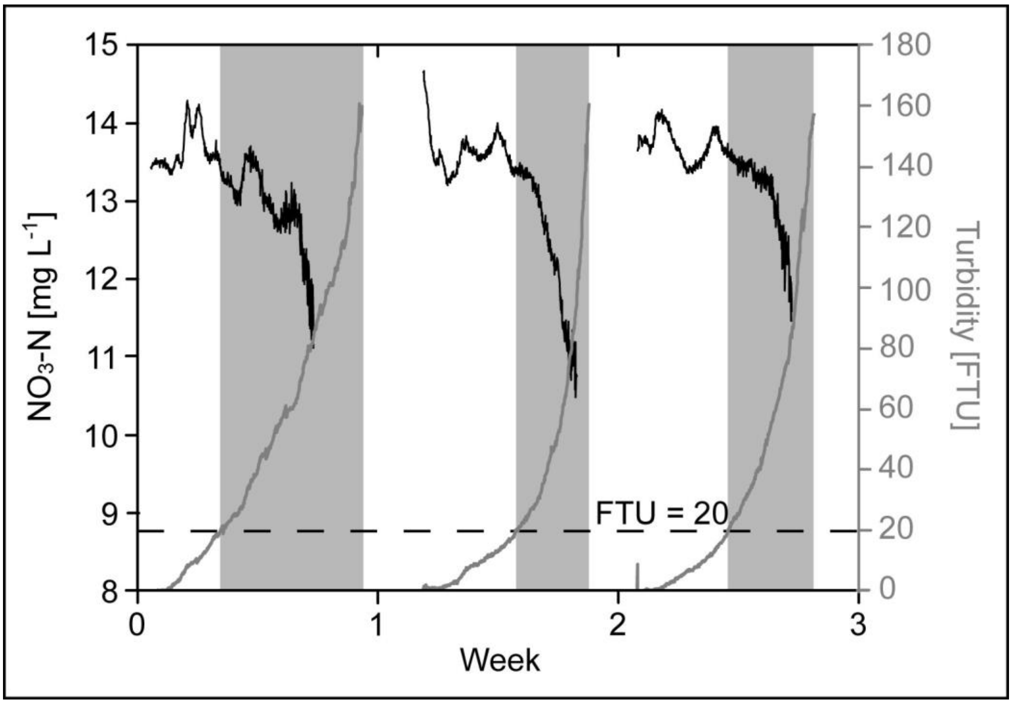

Fig. 5: Interference of deposition of suspended matter at the measuring path of the multiple wavelength spectrophotometer (MWS) due to vertical installation of the sensor. The grey areas indicate the time range when the FTU signal is ≥ 20 and thus the reported NO_3-N concentrations are not reliable during that time. Reporting of NO_3-N concentrations breaks down at 80 FTU.

Tab. 1: Description of the double wavelength spectrophotometer (DWS) and the multiple wavelength spectrophotometer (MWS).

Components	**DWS**	**MWS**
Hardware	• Sensor incl. wiper for cleaning, cable, handling device (station terminal) • Internal memory included	• Sensor, cable, handling device (station terminal) • Internal memory included
Hardware options	• Flow through-unit • GSM modem • Mobile display for on-site operations • Additional analogue outputs for up to 8 sensors	• Cleaning device necessary in natural waters • GSM modem • Additional analogue outputs (terminal) • Interfaces for 1 MWS and 3 other sensors
Software options	• WINXP-based • Remote control • Alarm option • Display on-site: concentrations and daily or weekly trend line over time • Password for protection of display possible	• WINXP-based • Remote control • Calibration menu for on-site calibration • Alarm option • Display on-site: switching between nitrate concentrations over time and spectra • Automated light source check
Output	• Absorption values at EM and ER • Calculated NO_x-N concentrations • Output via memory card and/or remote control	• Absorption spectra • Calculated NO_3-N concentrations • Output via memory card and/or remote control
Maintenance	• Low • Manufacturers calibration of sensor needs to be refreshed after 1 – 2 years	• Low • After 2 years check of light source at the manufacturer necessary (cost intensive ~ 1.000 € excl. VAT)
Warranty	• 5 years on light source	• 3 years
Costs	• Low maintenance and labour costs • Purchase price: ~ 16.000 € excl. VAT	• Low maintenance and labour costs • Purchase price: ~ 20.000 € excl. VAT

Tab. 2: Evaluation of appliance of the double wavelength spectrophotometer (DWS) and the multiple wavelength spectrophotometer (MWS): positive (+), negative (–) and neutral (o) aspects

Positive, negative and neutral aspects		**DWS**	**MWS**
Installation	+	• Easy • A L-bracket provided by the manufacturer makes it simple to install the instrument in the correct position	• Easy
	–		• Must be aware that the measuring path needs to be orientated in a horizontal position with the measuring path down especially if used without cleaning device
Requirements	–	• Power source needed for operation	• Power source needed for operation
Calibration	+	• Easy if water matrix is similar to standard solutions provided by the manufacturer	• Off-site calibration provided by the manufacturer and site specific on-site calibration possible offering higher precision • Recalibration of the raw dataset possible
	–	• Only 2 point calibration possible for the user • On-site calibration complicated if water matrix differs significantly from standard solutions provide by the manufacturer or if collection of water samples representing the monitored NO_3-N range remains difficult	• Achievement of a sufficient level of expertise is necessary if off-site calibration is not useful • On-site calibration complicated if water matrix differs significantly from standard solutions provide by the manufacturer or if collection of water samples representing the monitored NO_3-N range remains difficult
Error detection	+	• Relationship Delta E to calculated concentration gives possibility for detection	• First derivative of spectra gives more detailed information, e.g. if values between 220 and 240 nm are positive, light or energy source is damaged
	–	• Dependence on manufacturer for provision of additional information	• Dependent on help of the manufacturer

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