Development of a robust nitrate sensor for online measurements

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Abstract

According to the EU Water Framework Directive the emission of nutrients and plant protection products to water bodies should be reduced dramatically. In practice threshold values for water bodies are exceeded due to leakages, discharges and unexpected problems from greenhouse facilities. Nitrate eutrophicates surface water. In the Netherlands nutrient solution recirculation in soilless cultivation is obliged and discharge is regulated to yearly crop specific nitrogen concentrations. However, water authorities still measure exceedances in surface water, leading to an interest real-time measurement of nitrogen or nitrate to have data faster available. Adjustments in nutrient recipes in greenhouses are based on a 7-14 days analysis of drainwater by sending it to a laboratory. This practice is suboptimal since the loss in nutrients is higher than necessary and it might even reduce crop development. Besides it is time consuming and often expensive. In areas where the results of the laboratory are not fast available, a nitrate sensor may even play an important role in creating the right solution for the plants. With a real-time measuring nitrate sensor, it is possible to fertigate more accurately which increases the harvest/quality of the crop with a lower environmental footprint. Besides, such a nitrate sensor has also a large scientific value since the dynamic nitrate uptake by the crop can be studied at a scale of minutes instead of days. A start has been made to analyse available methods for measuring nitrate, and in this study we will present an innovative optical fibre based nitrate sensor using an algorithm which has been tested in a greenhouse setting at field conditions. This UV-VIS spectroscopy system in combination with the developed model can be used for online monitoring of nitrate concentrations in hydroponic solutions, without the use of any reagents or need for recalibration, to enhance the efficiency and safety of greenhouse systems with respect to water reuse and recycling.

Keywords: hydroponics, sensors, discharge, eutrophication, UV-VIS, PLS, surface water

INTRODUCTION

Worldwide, in many regions with protected horticultural activities, threshold values for nitrate in water bodies are exceeded due to leakages, discharges and unexpected problems from greenhouse facilities. As an example, in southeastern Spain aquifers are contaminated with nitrate leached from greenhouses which predominantly contributes to the eutrophication of surface water (Thompson et al., 2020). In the Netherlands recirculation is mandatory for soilless cultivation systems and discharge is regulated according to crop specific nitrogen concentrations. Despite these regulations water authorities still measure exceedances of nitrate in surface water in the vicinity of greenhouses (van der Salm et al., 2020).

Nitrate levels in drainage and discharges from greenhouses can be minimized by monitoring the nitrate concentration in the greenhouse extensively. Adjustments in nutrient recipes in greenhouses are based on weekly/bi-weekly laboratory analysis of the nutrient solution around the roots. This practice is suboptimal since nitrate levels at the roots deviate from the desired values in such a way that nitrate losses are higher than necessary which might even reduce crop development (Gieling et al., 2012). In addition, laboratory analysis can

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be time consuming, expensive or not even available in some areas. With a real-time measuring nitrate sensor it is possible to optimize fertigation which increases the harvest or quality of the crop with a lower environmental footprint.

Commonly used in situ sensing technologies for real time analysis of nitrate in aqueous solutions are ion selective electrodes dip probes (ISE) and optical sensors based on UV-visible (UV-VIS) spectroscopy. UV-VIS spectroscopy has shown to be more effective over ISE sensors since the measurements are hardly influenced by pH, temperature or other anions (Edwards et al., 2001; Yeshno et al., 2019). UV-VIS spectroscopy measures the amount of UV-light absorbed by an aqueous sample in a cuvette. The absorbance of UV-light by the sample depends on the concentrations of the absorbing components in the solution. Several methods exist to determine the nitrate concentration from the measured absorbance. Most are based on simple direct linear models and use the strong absorbance band of nitrate around 200-220 and 300-310 nm, respectively, which are more sensitive for low nitrate concentrations and nitrate concentrations higher than 0.2 g L^{-1} (Thomas and Burgess, 2017; Yeshno et al., 2019).

Dissolved organic matter (DOC) strongly interferes with nitrate analysis by UV-VIS spectroscopy since it also absorbs UV-light. Therefore, direct linear models cannot be applied in this case. A two-wavelength approach can account for DOC by correcting the measured absorbance at 200/220 nm with an absorbance measurement at 275/300 nm (Armstrong, 1963; Edwards et al., 2001). In addition, several multilinear regression models (PLS, PCA) in combination with pre-treatment methods have been developed to exploit the entire UV spectrum in order to deal with interferences of DOC on nitrate detection (Karlsson et al., 1995; Thomas et al., 2014).

So far UV-VIS spectroscopy has shown to be an effective and simple method for the detection of nitrate and accounting for DOC in natural water bodies, waste water and soil pore moisture without the use of any reagents (Rennie et al., 1979; Sarraguça et al., 2009; Avagyan et al., 2014; Causse et al., 2017; Thomas and Burgess, 2017; Yeshno et al., 2019). The existence of a method to measure nitrate in different hydroponic solutions and accounting for (DOC) interferences has not been described yet. Therefore, we present a novel comprehensive approach to measure nitrate in hydroponic solutions with UV-VIS spectroscopy which has the potential to enhance the efficiency and safety of greenhouse systems with respect to water reuse and recycling.

MATERIALS AND METHODS

Experimental setup

The UV-VIS spectroscopy system which has been used for the experiments is visible in Figure 1. The hydroponic solution was pumped through a flow cell containing a 10 mm cuvette. The measuring system contains a deuterium light source (Ocean Optics model DH-2000-BAL), a spectrometer (Ocean Optics model HR4000) with a slit reflection probe and optical fibres. It measures the light intensity between 187 and 667 nm.
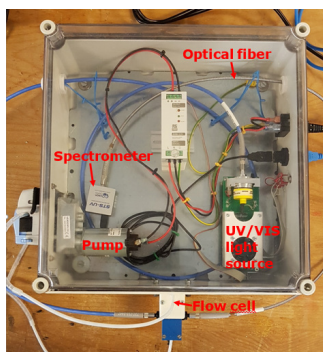

Figure 1.   The UV-VIS spectroscopy system containing a pump, optical fibres, a spectrometer and a light source.

Since hydroponic solutions contain various ions which might cause interferences with the nitrate measurement, a Hoagland solution (Hoagland and Arnon, 1938), which is one of the most standard hydroponic solution, was used as a reference solution (Table 1).

Table 1. The composition of the Hoagland solution.

	Concentration	Unit
EC	1.0	mS cm^{-1}
pH	5	-
NH_4^+	<0.1	mmol L^{-1}
K^+	1.1	mmol L^{-1}
Na^+	<0.1	mmol L^{-1}
Ca^{2+}	2.5	mmol L^{-1}
Mg^{2+}	2.2	mmol L^{-1}
NO_3^-	5.2	mmol L^{-1}
Cl^-	0.2	mmol L^{-1}
SO_4^{2-}	2.1	mmol L^{-1}
HCO_3^-	<0.1	mmol L^{-1}
PO_4^{2-}	1	mmol L^{-1}
Fe	26	μmol L^{-1}
Mn	7.4	μmol L^{-1}
Zn	0.9	μmol L^{-1}
B	44	μmol L^{-1}
Cu	0.4	μmol L^{-1}
Mo	0.37	μmol L^{-1}

First the absorption of 20 samples was measured to examine whether the measured absorbance values at all wavelengths were reproducible. In total 74 samples were collected for a period of 7 months consisting of supply (44) and drain (20) solutions from growing systems with various crops and consisting of surface water from greenhouse areas (10). At the day of measuring a duplicate sample was sent to an accredited laboratory which measured the nitrate concentration by inductively coupled plasma (ICP). With the known nitrate concentrations, the measured light intensities of the samples and the reference solution, the system was calibrated, which process is described in the next paragraph.

Theory

From the measured light intensities of the samples and the reference solution the absorbance was calculated via the Lambert-Beer equation:

$$A = -\log_{10} \frac{I}{I_0} \tag{1}$$

where I represents light intensity after passing through the water sample, and I_0 the measured light intensity after passing through the reference solution. Lambert-Beer's law describes a linear relation between the absorbance and the concentration of a pure component. Since greenhouse water might contains several UV absorbing components, like organic material from the substrate (coir and peat), plant protection products, root exudates, degrading parts from roots, leaves and fruits, a direct linear model cannot be used.

Partial least squares (PLS) is a multivariate statistical method to determine the concentration of a single component in complex solutions (Haaland and Thomas, 1988; Brereton, 2003; Langergraber et al., 2003; Mark and Workman, 2007; Sarraguça et al., 2009; Lepot et al., 2016). To use PLS, the measured absorbance should be normalized to reduce overlapping peaks to allow for a better quantification of the individual components (Karlsson et al., 1995; Thomas and Burgess, 2017). A common way for normalizing spectral data are to calculate the 2nd order derivative of the absorbance values according to:

$$\frac{d^2 A_\lambda}{d\lambda^2} = \frac{A_{\lambda-h} + A_{\lambda+h} - 2 \cdot A_\lambda}{h^2} \qquad (2)$$

with h as differentiation step (10 nm), A_λ the absorbance value at wavelength λ and $A_{\lambda-h}$ the absorbance value at wavelength λ-h (Thomas and Burgess, 2017). With the 2nd order derivative of the absorbance values and the known concentrations of the 74 samples, a PLS regression was made which was used as calibration for the sensor system. The entire procedure of data progressing and executing the PLS regression was done with Matlab (2018b).

Validation

Since overfitting is a reported problem with PLS regressions (Crumpton et al., 1992), an experimental plan was set up containing 7 different tests to determine the accuracy of the calibration model (Table 2).

Table 2. The description of the validation experiment.

Test	Description
A	KNO$_3$ solution with different NO$_3^-$ concentrations: 2, 5, 10, 15 and 25 mmol L^{-1} at the same EC of 3.0 mS cm^{-1}. KCl has been used to reach the desired EC
B	KNO$_3$ solution with a constant NO$_3^-$ concentration of 15 mmol L^{-1}, but with different ECs: 2.0, 2.5, 3.0 and 3.5, 4.0. KCl has been used to reach the desired EC
C	Standard tomato, cucumber and strawberry nutrient solution with the same EC and nitrate concentration which variates from Hoagland solution (Table 1)
D	Standard tomato nutrient solution containing illite (6 mg L^{-1}), but with different concentrations of humic acid: 5, 10 and 15 mg L^{-1}
E	Standard tomato nutrient solution containing humic acid (10 mg L^{-1}), but with different concentrations of illite: 3, 6 and 9 mg L^{-1}
F	Solutions of test D filtered (pore size: 2 μm)
G	Solutions of test E filtered (pore size: 2 μm)

In each test the nitrate concentration was measured with the calibrated UV-VIS sensor and the measurement was compared with the result of the laboratory to determine the accuracy of the UV-VIS sensor. The samples in the above test are not included in the calibration.

Test A and B were set up to test the interaction between the EC and the measurement of the sensor. The purpose of test C was to examine the influence of a different matrix of ions on the nitrate measurement. Samples of test D and E contain illite and humic acid to mimic, respectively, turbidity and organic material in greenhouse water (van Ruijven et al., 2014). The results of test F and G were compared with test D and E to see the effect of suspended particles on the measurement.

Based on communication with several growers, the desired accuracy, which is defined as the difference between the lab measurement and measurement of the sensor, should be maximum 10% in order to use the sensor for adapting the nutrient solution around the roots.

RESULTS AND DISCUSSION

Calibration

After the repetitive measurements it becomes clear that the measured absorbance values below 260 nm and above 540 nm were not reproducible, so those wavelengths were excluded from the calibration. In Figure 2 the predicted concentration of nitrate in the 74 samples is plotted versus the reference concentration measured by the laboratory. There is a very good correlation between measured and predicted concentrations of nitrate.
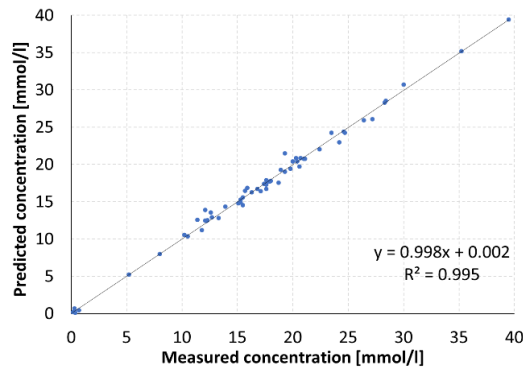
Figure 2. The predicted and measured concentration of nitrate plotted for samples A until E and the calibration.

Validation test

The results for test A until E are plotted in Figure 3A-E. Figure 3A displays a good correlation between the measured nitrate concentration of the sensor and the measured nitrate concentration by the lab. The slope shows that the sensor underpredicts the nitrate concentration with 8% on average, but the accuracy is lower for sample A1 which has a low nitrate concentration. The reason is that the calibration model makes a correction for other supposed UV-light absorbing constituents, but since nitrate is the only constituent which absorbs UV-light in the samples results in a correction which is not necessary.

The results of test B (Figure 3B) also clearly show a strong correlation between the measured nitrate concentration of the sensor and the measured nitrate concentration by the lab. Again the sensor underpredicts the nitrate concentration with 8%. Since this underprediction was constant for all samples it is evident that the nitrate measurement is not affected by the EC. In addition, the chloride concentration in samples B1 until B5 was in the range of 0-20 mmol L^{-1}, so the measurement of the sensor is clearly not influenced by the chloride concentration as well.

The sensor is also able to measure the nitrate concentration in three hydroponic solutions which contain no organic matter, see Figure 3C. The sensor can clearly distinguish 18, 17 and 14 mmol L^{-1}. Moreover, the ionic composition of the samples was slightly different but the sensor is still able to measure the nitrate content in the samples.

As mentioned before hydroponic solutions can be turbid and can contain dissolved organic matter. To see what the influence of organic matter is test D was carried out, see Figure 3D. It is evident that there is no correlation between the measured concentration of the lab and the sensor. Even though D2 and D3 have the same nitrate concentration, the sensor measured a higher nitrate concentration in sample D3 which has the highest humic acid (DOC) concentration. So the presence of DOC definitely has an influence on the nitrate measurement. Since the data set used for the calibration contains relatively more samples of supply water than drain water, it is to be expected that the results from test C are better than the results of test D. Although there is a low correlation between the measured concentration of the sensor and the concentration measured by the lab, the accuracy of the above samples is still within the desired 10% which is a promising result. The accuracy of the sensor can be increased when more drain samples containing dissolved organic matter will be used for the calibration.

The results of test E (Figure 3E) also show no correlation between the measured nitrate concentration of the sensor and the measured concentration by the lab. Even though the turbidity and the nitrate concentration increase from E1 to E3, the measured concentration by the sensor remains constant (±12.8 mmol L^{-1}). This could indicate that turbidity masks the nitrate measurement. So despite of an accuracy below the desired 10% it cannot be confirmed that the sensor can cope with varying turbidity levels perfectly. More tests should be performed to examine the influence of turbidity and to improve the sensor measurement. To see the effect of filtering the sample test F and G are performed (Figure 4).
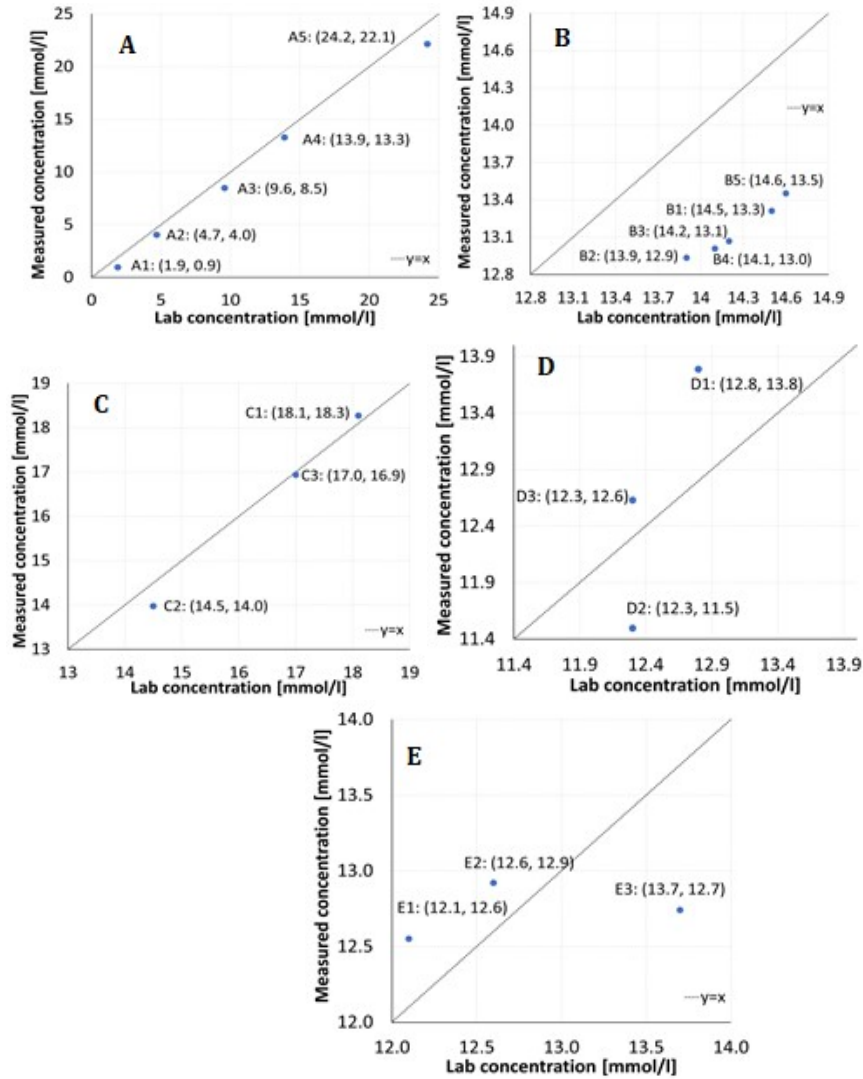
Figure 3. The concentration determined by the laboratory and the measured nitrate concentration by sensor plotted for samples A until E. Description of the nutrient solution A until E are reported in Table 2.
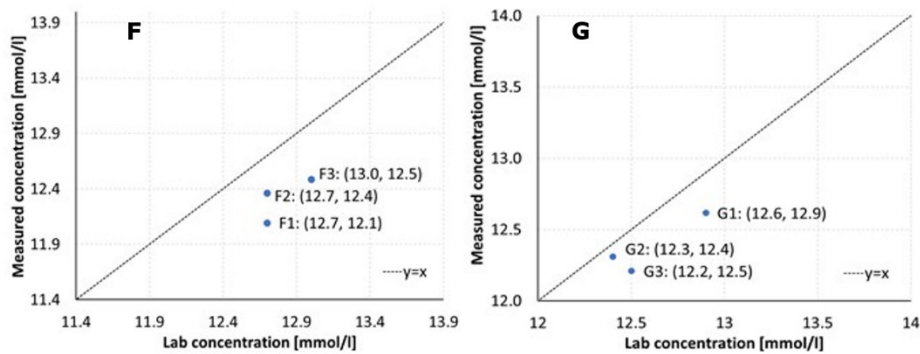

Figure 4. The concentration determined by the laboratory and the measured nitrate concentration by sensor plotted for samples F until G.

The results of test F and G are significantly better compared to test D and E since the accuracy lies between the 5 and 1% so filtering the samples improves the results. This shows that the samples contain suspended particles larger than 2 μm which have an influence on the measurement. Probably a smaller filter size could improve the results even further, since the measurements of test C (samples without organic material) were very good. Further tests should confirm this.

It is remarkable that the measured concentration by the laboratory between E3 and G3 is significantly different. From experience we also know that the results of the analytical labs are not always 100% accurate, so this should also be kept in mind. In general, turbidity and dissolved organic matter content in the hydroponic samples D, E, F and G were mimicked with respectively illite and humic acid. For this paper it is assumed that the absorption spectrum of these constituents is the same as for dissolved organic matter found in hydroponic solutions but this should be confirmed with more extensive tests.

The method explained above can also be applied to measure nitrate in surface water. However, the absorbance band of nitrate around 200-220 nm is more sensitive for low nitrate concentrations, but the used UV-VIS system cannot measure absorption in that range properly. So in order to measure nitrate in surface water quantitatively some adaptations to the current system should be made. Nevertheless, the results of test A1 shows that it could be possible with the current sensor to measure at concentrations of 1 mmol L^{-1} (63 mg L^{-1}), which is close to the WHO standard for nitrate (50 mg L^{-1}). Therefore, the sensor with the current calibration model can also potentially be used as a qualitative method for nitrate measurements in surface water if more samples in the range of 0.5-1 mmol L^{-1} NO_3^- are included in the calibration.

CONCLUSIONS

An advanced model has been developed which can be used to measure nitrate in hydroponic solutions with UV-VIS spectroscopy. To examine whether this calibration model can account for the most common interferences in hydroponic solutions, several tests are performed. The results show that the nitrate measurement is not influenced by EC or ionic composition. DOC and turbidity have a small influence on the nitrate measurement, but all the results are within the desired 10% accuracy. However, more extensive tests should be performed to get a better understanding of the effect of dissolved organic carbon and turbidity on the nitrate measurements.

The UV-VIS spectroscopy system in combination with the developed model can be used for online monitoring of nitrate concentrations in hydroponic solutions, without the use of any reagents or need for recalibration, to enhance the efficiency and safety of greenhouse systems with respect to water reuse and recycling.

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