Long-term evaluation of a spectral sensor for nitrite and nitrate

L. Rieger, G. Langergraber, D. Kaelin, H. Siegrist and P. A. Vanrolleghem

ABSTRACT

A spectral in-situ UV sensor was investigated to measure nitrite and nitrate concentrations in the effluent of the EAWAG pilot-scale plant. The sensor was used with a calibration that was based on data from another WWTP and was operated over a period of 1.5 years. The results showed constant accuracy although the sensor was operated with minimal maintenance (manual cleaning once a month). It could be shown that the sensor was able to accurately predict the nitrite and nitrate concentration with a precision of 0.32 mg N/l (95% prediction interval at mean lab value of 1.15 mg N/l) and 1.08 mg N/l (at 5.55 mg N/l) for nitrite and nitrate, respectively. The UV sensor showed good results for nitrite in the low concentration range and very accurate results for higher concentrations (up to 10 mg N/l). This allows using the sensor for alarm systems as well as for control concepts at WWTPs.

Key words | in-situ sensor, long-term, nitrate, nitrite, on-line, UV spectroscopy

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INTRODUCTION

Nitrite is an intermediate product of the two-step process of nitrification. Since the second step of nitratation is very fast, the nitrite concentration in the effluent of a WWTP is normally very low (around 0.1 mg/l). Enrichment of nitrite in the system usually suggests that the microbiological processes are disturbed, i.e. they are inhibited due to toxic substances or to unfavourable conditions for the nitrite oxidiser. Since nitrite is a strong poison for fish, high nitrite concentrations in the effluent of WWTPs can lead to damage to organisms if the dilution of the receiving water body is too low.

Since laboratory measurements of grab samples can give only a snapshot picture and the analysis of 24 h-composite samples is critical due to the unstable nitrite concentration, their meaningfulness is limited. The use of on-line analysers, which need a high sample preparation time, can lead to similar problems. In-situ sensors would therefore be advantageous in this case.

Nitrate, beside ammonia, makes up the major part of the total nitrogen concentration in the effluent of WWTPs and is therefore an important operational indicator and is also often used for legislation purposes. Measuring both parameters on-line will increase the monitoring capability and therefore enable appropriate control of the plant in order to prevent ecologically harmful discharges. Measuring them with a single probe will reduce the effort and therefore the costs.

Starting with first tests in 2003 (Rieger *et al.* 2004) a spectral in-situ sensor was tested over a period of one and a half years in the effluent of a pilot plant in Switzerland. The sensor provides measurements of spectra between 210 and 400 nm (UV range) for every measuring cycle. The goal was to analyse i) the long-term robustness of the optical equipment and ii) the calibration stability of the underlying spectral analysis model.

The optical equipment is exposed to the difficult environmental conditions of a WWTP and therefore the

problem of aging of light source and detector or changes in the optical path (e.g. due to scratches or precipitation on the optical lenses) could cause measuring errors.

The second question was to determine whether the calibration is stable over a prolonged period. It should be kept in mind that the applied method is not directly measuring nitrate or nitrite but some spectral information. Although nitrate and nitrite have known peaks in the spectra (around 200–250 nm, see Figure 1), the system has to deal with interferences stemming from organic matter and other disturbing ions which show an absorption in the same wavelength range or particles that block the optical measuring path. Since the interferences are of different magnitude for different water matrices, the calibration stability is not guaranteed.

MATERIAL AND METHODS

The tested in-situ spectrometer (spectro::lyser, s::can Messtechnik GmbH, Vienna, Austria) measures the absorbance of ultraviolet light (UV from 210 to 400 nm) with a path length of 10 mm designed to enable differentiation between nitrite and nitrate at TSS concentrations up to 15 mg/l (manufacturer's specification). Physically, 256 wavelengths are measured between 210 and 400 nm (resolution ca. 0.8 nm) and these are converted to a resolution of

1 nm for calculating the concentrations. A single evaluation of the entire spectrum typically takes 15 seconds. Measuring the UV absorbance is an indirect method of determining water compounds. In principal, the sensor can be calibrated for all absorbing substances, typical applications in the water sector being measuring concentrations of organic matter, nitrate and nitrite (Figure 1).

The spectrometer is constructed as a compact submersible sensor which enables optical spectra to be measured directly in liquid media with an accuracy approaching laboratory analysis quality. The spectrometer is equipped with an auto-cleaning system using pressurized air which has been proved to be extremely reliable (Gruber *et al.* 2006). More information about the sensor can be found in Langergraber *et al.* (2003) and van den Broeke *et al.* (2006).

For typical waters (e.g. municipal wastewater – raw and treated, river water, drinking water etc.) the manufacturer provides a so-called *global calibration* as a default configuration of the in-situ spectrometer. To enhance the precision, a *simple local calibration* that is based on grab samples analysed in the lab has to be carried out that considers the different composition of the wastewaters to be analysed. By performing a *local PLS (Partial-Least-Square) calibration* one can improve trueness, precision and long-term stability of the results by finding a set of wavelengths better adapted to the matrix of specific wastewater (Rieger *et al.* 2006).
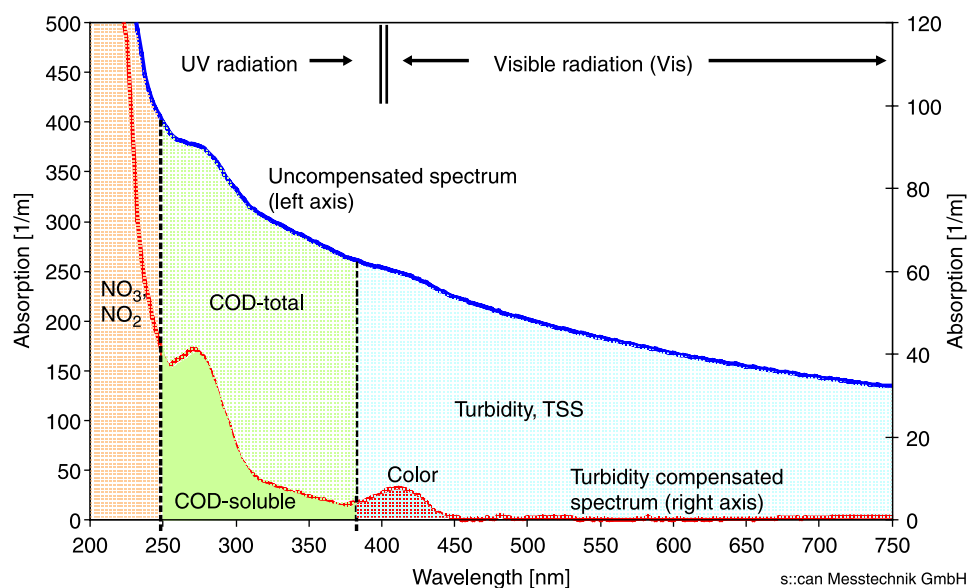

Figure 1 | Absorption of different compounds within the spectrum from 200 to 750 nm (van den Broeke *et al.* 2006).

Effluent of EAWAG pilot plant

The EAWAG pilot-scale wastewater treatment plant (Switzerland) treats the wastewater of approx. 70 p.e. ($\approx 27\,m^3$/d inflow) and receives municipal wastewater mixed with an unknown amount of industrial discharge. It is operated for carbon removal, full nitrification and pre-denitrification. The goal of the study was to evaluate different DO control options and especially the influence of low concentrations of dissolved oxygen in the biological stage on possible accumulation of nitrite in the effluent and measures to control it by means of changes to the aeration intensity.

The spectrometer was installed in the effluent of the secondary clarifier and used the calibration settings of a local PLS calibration that was based on a data set from another WWTP (Thunersee, Switzerland) plus lab experiments with standard addition on different matrices (Rieger *et al.* 2004). For the reference analysis, grab samples were taken directly beside the sensor and analyzed in the EAWAG laboratory. The working range of the sensor was between 0 and 7.55 mg NO_2-N/l and 0 to 14.8 mg NO_3-N/l with median values of 0.4 mg NO_2-N/l and 5.7 mg NO_3-N/l, respectively. To test the sensor accuracy also for higher concentrations, measurements from a spiked vessel (normal effluent water matrix with addition of a high concentrated stock solution) were taken from time to time.

During the start-up phase (winter 2004/2005) an additional on-line analyser with in-situ filtration unit (Tres-Con NO_2, NO_x, in combination with PurCon IS, WTW, Weilheim, Germany) was installed in the effluent of the secondary clarifier of the EAWAG pilot plant to compare the results from wet-chemistry (nitrite) and on-line UV analysis ($NO_x = NO_2 + NO_3$) with the spectral in-situ sensor.

Lab analysis

The reference measurements for nitrite and nitrate were carried out in the EAWAG laboratory using the flow injection analysis method (FIA, ASIA, Ismatec AG, Glattbrugg, Switzerland) and an ion chromatograph (761 compact IC, Metrohm AG, Herisau, Switzerland) depending on the measuring range.

Evaluation procedure

For the evaluation of the sensor uncertainties based on comparative measurements a procedure according to Rieger *et al.* (2005) was used.

RESULTS AND DISCUSSION

Validation of the sensor calibration

Directly after installation at the EAWAG pilot plant, experiments were carried out to check whether the Thunersee calibration is also applicable at the new location. The sensor was put into a vessel with effluent wastewater and a number of standard additions were carried out, taking grab samples from each addition step. With this procedure it should be tested whether the sensor is able to detect higher nitrite concentrations with sufficient accuracy (as the project deals with increased nitrite concentrations). For nitrite these experiments showed excellent results, while for nitrate an offset occurred that could be eliminated by a simple local calibration, as described by Rieger *et al.* (2006).

Figures 2 and 3 show the comparative measurements for nitrite and nitrate, respectively, grouped into several time periods: the December 2004 data from the validation experiments and three 6-months periods during the operation of the sensor. For nitrite (Figure 2) the highest concentrations
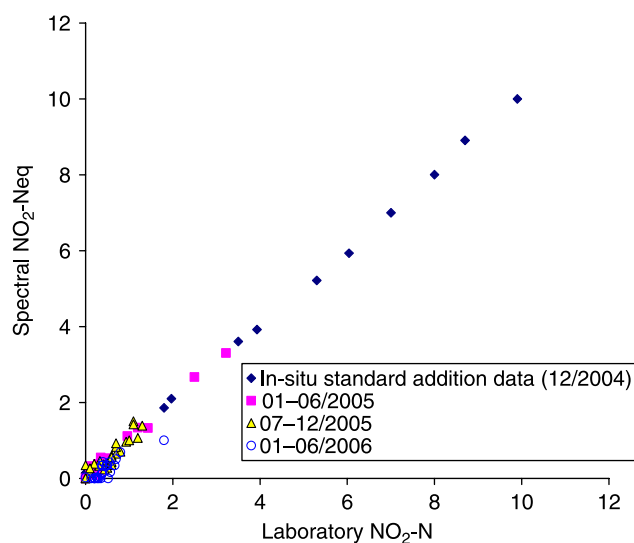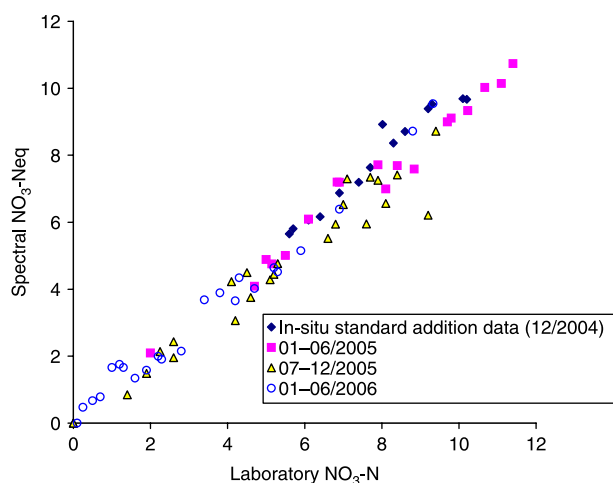

Figure 2 | Validation data for nitrite grouped into different time periods.

Figure 3 | Validation data for nitrate grouped into different time periods.

occurred at the beginning of the validation experiments. A higher accuracy at the higher nitrite concentrations that occurred frequently during the validation period can be observed. This indicates that the sensor is an excellent instrument to monitor nitrite effluent concentrations with high accuracy.

For nitrate (Figure 3) the validation experiments took place at higher concentrations between 5 and 10 mg

NO_3-N/l. Over time the validation data also showed good agreement between lab and sensor measurements at lower concentrations.

Long-term evaluation

The sensor was placed in the effluent of the EAWAG pilot plant in December 2004. Reference samples for analyses in the laboratory have been taken on a regular basis, in total about 90 reference samples. The measurements lasted for a period of 1.5 years until the end of June 2006. Maintenance was limited to manual cleaning once a month.

Figure 4 shows sensor and lab data for the 3-months period April to June 2005. One can see that the EAWAG pilot plant was operated with special experimental objectives as particularly high nitrite concentrations could be observed. In general, the lab data validated the sensor data, especially for nitrite. Lab nitrate measurements too showed a good agreement with the sensor data.

Figures 5 and 6 show the validation for nitrite and nitrate based on measurements in the effluent of the EAWAG pilot plant, respectively. The 95% prediction interval for nitrite was ± 0.32 mg NO_2-N/l at a mean lab
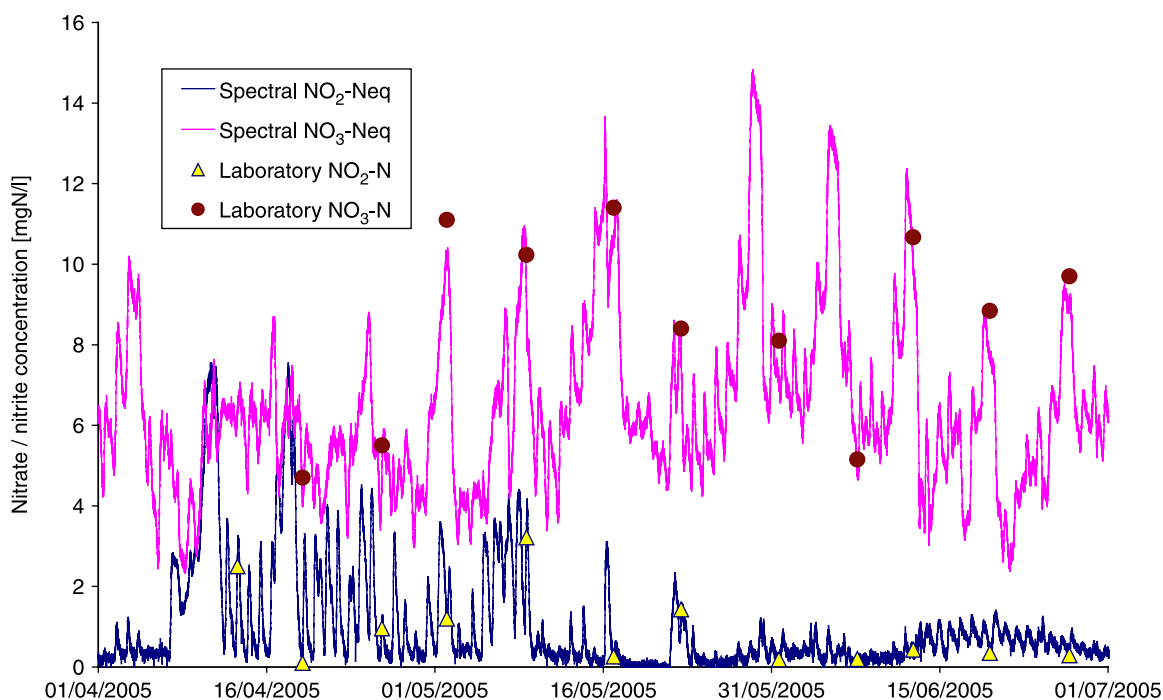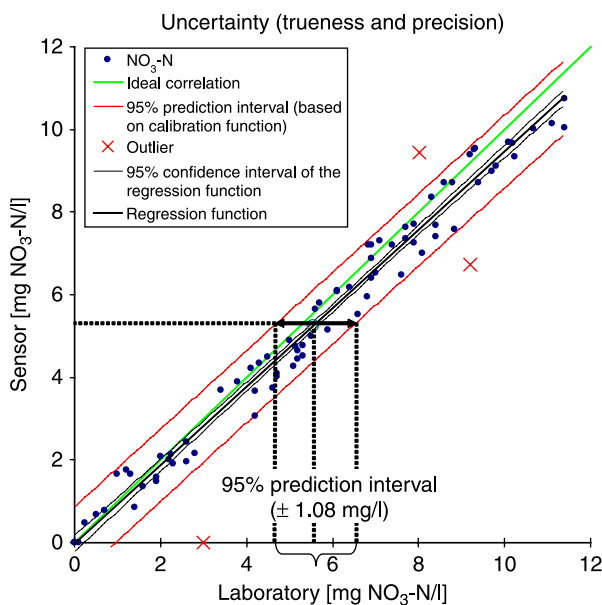

Figure 4 | Comparison of sensor and lab data from April to May 2005.
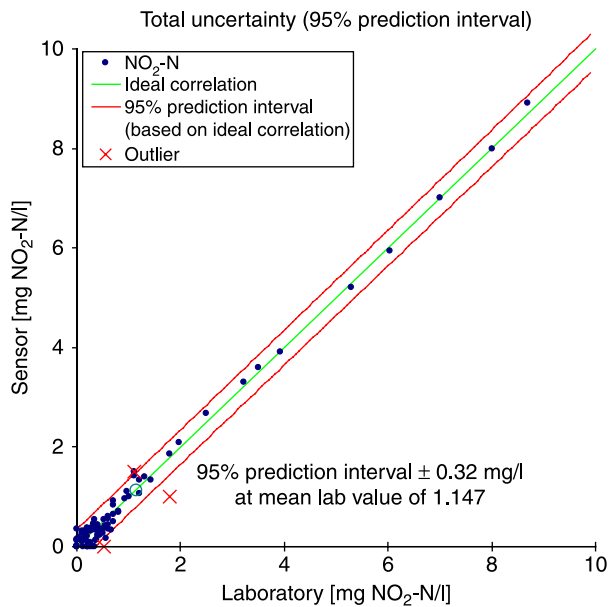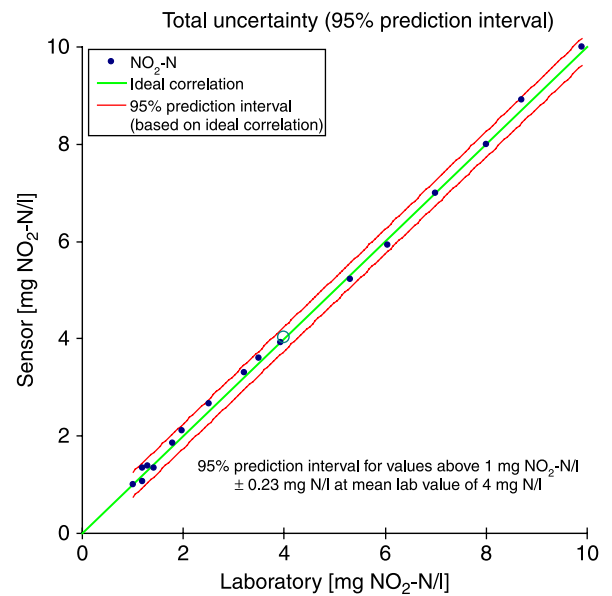
Figure 5 │ Validation data for nitrite based on WWTP effluent samples with a 95% prediction interval (width = ± 0.32 mg/l at a mean lab value of 1.15 mg NO_2-N/l).

Figure 7 │ 95% prediction interval for nitrite for values above 1 mg NO_2-N/l (width = ± 0.23 mg/l at a mean lab value of 4 mg NO_2-N/l).

value of 1.15 mg NO_2-N/l. This is an extremely good result especially given the low maintenance of this in-situ sensor. Note that for concentrations above 1 mg N/l the prediction interval is even smaller (± 0.23 mg NO_2-N/l at a mean lab value of 4 mg N/l, see Figure 7). The clouds of data in the

Figure 6 │ Validation data for nitrate based on WWTP effluent samples with a 95% prediction interval (width = ± 1.08 mg/l at a mean lab value of 5.55 mg NO_3-N/l).

lower concentration range, indicating lower data quality, are also related to the higher uncertainty of the lab measurements in this range.

For nitrate the 95% prediction interval was ± 1.08 mg NO_3-N/l at a mean lab value of 5.55 mg NO_3-N/l. The broader prediction interval compared to the nitrite measurements cannot be sufficiently explained. The same device and the same wavelength ranges are used for nitrite and nitrate and therefore problems with particles or other clogging effects can be excluded. Other calibrations based on different wavelengths did not provide better results. Since also the TresCon on-line UV analyser shows comparable prediction intervals of ± 1.47 mg/l (see below, Figure 10) two hypotheses can be drawn: i) the low precision is caused by the measuring principle and by unknown interfering compounds in the water matrix or ii) the lab measurements are not accurate enough for the water matrix under evaluation. The lab equipment was carefully tested by carrying out standard additions on pure water as well as on different wastewater samples, but a changing matrix could still have caused uncertainties of the measurements.

Figure 8 shows the residuals (sensor minus lab value) for nitrite and nitrate over time. Starting in March 2006 a drift is visible for nitrite as well as nitrate. An evaluation of
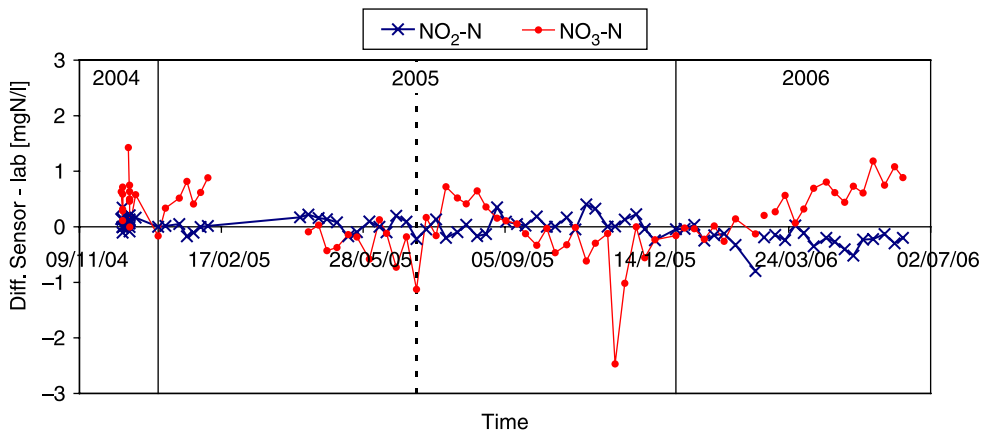
Figure 8 │ Residuals (sensor minus lab value) for nitrite and nitrate over time.

the sensor manufacturer revealed problems with the light source and therefore the probe had to be sent back to the supplier.

Comparison with on-line analyser

In winter 2004/2005 the spectral in-situ sensor was also tested against an on-line system using wet-chemistry (NO_2) and UV (NO_x), respectively, both after a filtration unit. Figures 9 and 10 show the results from comparative measurements (taking the response time of the on-line

system into account). Both nitrite (95% prediction interval $\pm$ 0.51 mg N/l at mean lab value of 0.45 mg N/l) and nitrate ($\pm$ 1.47 mg N/l at 4.3 mg N/l) show worse results than the results from the spectral sensor. The reason for the bad results of the wet-chemistry analyser could be related to the filtration unit, which causes a delay of approx. 10 min and, in addition, mixing of the sample in the fast loop tubes and other volumes of the sampling system. The result is that peaks are damped out by the system (see Figure 4).
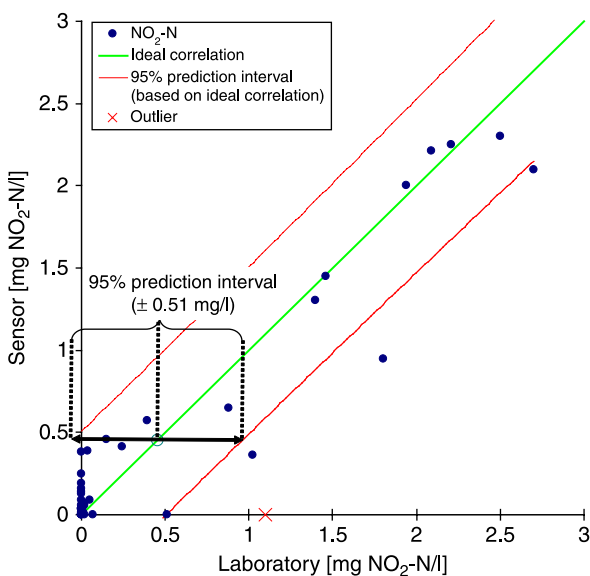
Figure 9 │ Wet-chemistry on-line analyser: Validation data for nitrite based on WWTP effluent samples with a 95% prediction interval (width = $\pm$ 0.51 mg/l at a mean lab value of 0.45 mg NO_2-N/l).
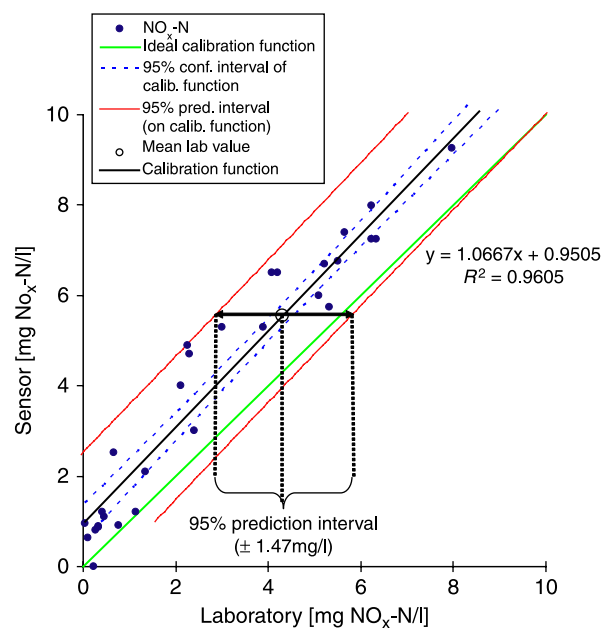
Figure 10 │ UV on-line analyser: Validation data for nitrate + nitrite (NO_x-N) based on WWTP effluent samples with a 95% prediction interval (width = $\pm$ 1.47 mg/l at a mean lab value of 4.3 mg NO_3-N/l).

The on-line UV analyser for NO_x has a limited number of wavelengths and therefore fewer options for individual calibration in comparison to the in-situ spectral probe. The off-set of about 1 mg/l is clearly a calibration problem. Since a first calibration with five standards (based on pure water) during start-up showed excellent results, the source of the problem is presumably related to the wastewater matrix with a strong industrial influence.

After three months of operation, it was decided to remove the on-line analyser and only rely on the optical probe due to its better performance and lower maintenance requirements.

CONCLUSIONS

A spectral in-situ sensor measures 256 wavelengths per measurement but only few wavelengths are used to correlate the spectral information to the nitrite respective nitrate concentrations in the liquid to analyse.

The tested spectral in-situ sensor was calibrated based on data from another WWTP and additional lab experiments (standard addition on wastewater matrix from the same WWTP). PLS regression was used to develop and calibrate the underlying multivariate model.

It could be demonstrated that the sensor was able to accurately predict the nitrite and nitrate concentration in the effluent of the EAWAG pilot-scale plant with a precision of $\pm$ 0.32 mg N/l (95% prediction interval at mean lab value of 1.15 mg N/l) and $\pm$ 1.08 mg N/l (at 5.55 mg N/l) for nitrite and nitrate, respectively. This proofs that the calibration developed for another WWTP is also applicable to other wastewater matrices.

Comparative measurements were carried out over a period of 1.5 years and the results showed constant accuracy except for the last three months where a drift occurred for nitrite as well as nitrate. The drift could be related to a problem with the light source, which was replaced by the manufacturer.

As a summary it can be stated that the long-term stability is excellent, especially since the sensor requires only a minimum of maintenance. A second on-line analyse with a filtration unit was tested but removed due to the better results of the in-situ sensor and the high demand of the on-line system in terms of consumption of chemicals and maintenance.

The sensor showed good results for nitrite in the low concentration range and even better results for higher concentrations (up to 10 mg N/l). This allows to use the sensor for alarm systems as well as for control concepts at WWTPs.

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