Experiences with a multi-parameter submersible UV/VIS spectrometer for monitoring a denitrification reactor system

A. Boley and W.-R. Müller

University of Stuttgart - Institute for Sanitary Engineering, Water Quality and Solid Waste Management – Task Group Biology - Bandtäle 2 – D-70569 Stuttgart (E-Mail: *angela.boley@iswa.uni-stuttgart.de*,)

Abstract
A multi-parameter submersible spectrometer system was applied to monitor the water quality of the in- and effluent of a denitrification reactor in drinking water treatment. The data obtained were compared with values from manual sampling. The results show that nitrate measurement with the system examined could help to survey the denitrification performance, whereas the nitrite measurement as part of the sensor evaluation is not yet reliable. DOC concentrations measured by the spectrometer were often not recovered in the lab, but the data basis is yet too small for consistent results.

Keywords
Denitrification, drinking water monitoring, in-situ measurement, nitrate / nitrite measurement spectrometer

INTRODUCTION

Biological denitrification is a process where bacteria reduce nitrate to nitrogen via nitrite. Under normal conditions, only low concentrations of the intermediate product nitrite will appear in the treated water. However, if the bacteria are inhibited, nitrate concentrations in the effluent will increase and large nitrite amounts may suddenly appear. Monitoring of those denitrification processes especially in biological drinking water treatment is therefore a crucial point (European Standard 0,1 mg/L NO_2^-), due to limited resources of time and money for classical analysis.

For this reason, an online-measurement system for nitrate and nitrite monitoring could be an important tool. We report here about our experience with a new instrument, which is said to be able to measure nitrate and nitrite simultaneously online and in situ.

METHODS
Reactor installation
A semi-technical denitrification reactor with PCL (a biodegradable synthetic polymer) as carrier and carbon source was installed (fig. 1). The influent ("In") to the reactor was ground water supplemented with NO_3^-, PO_4^{3-}, Fe, and Mo stemming from stock solutions introduced in a mixing tank. Nitrite was not detectable in the influent.

Instrument
UV-Spectrophotometer (spectro::lyser, S::CAN Messtechnik GmbH, (Vienna, Austria) UV: 200 – 380 nm, path: 35 mm), reference medium: distilled water, we used ultra pure water. Data were collected (interval 1 min), stored (average value of 5 measurements) by a personal computer equipped with the software (ana::pro V4.0, S::CAN), and connected via RS 232 interface. Global calibration was provided by the manufacturer as described in Langergraber *et al*. (2003). Local calibration procedures as described in the software manual were carried out with nitrate, nitrite, and DOC.

Automatic Sampling

For monitoring the influent ("In") and effluent ("Out") water quality, computer controlled dosing pumps were installed to pump the water alternately from the mixing tank (influent) and the effluent vessel into a bypass fitting, where the sensor is installed. For data evaluation, values up to 10 min after and 2 min. before switching to the subsequent pump were dropped to avoid errors by remainders from preceding samples.

Lab analysis

Grab sampling was performed manually (sampling location see fig. 1). Nitrate and nitrite concentrations were determined by photometry, using Dr. Lange (Düsseldorf, Germany) cuvette tests LCK 340 (5….35 mg/L NO_3^- N), LCK 339 (0,23…13,5 mg/L NO_3^- N), LCK 341 (0.015…0.6 NO_2^--N) and LCK 341 (0.6…6 NO_2^--N) as described by the specific instructions for these tests. DOC was measured by Multi-N/C, AnalytikJena (thermocatalytic combustion principle) (Jena, Germany).
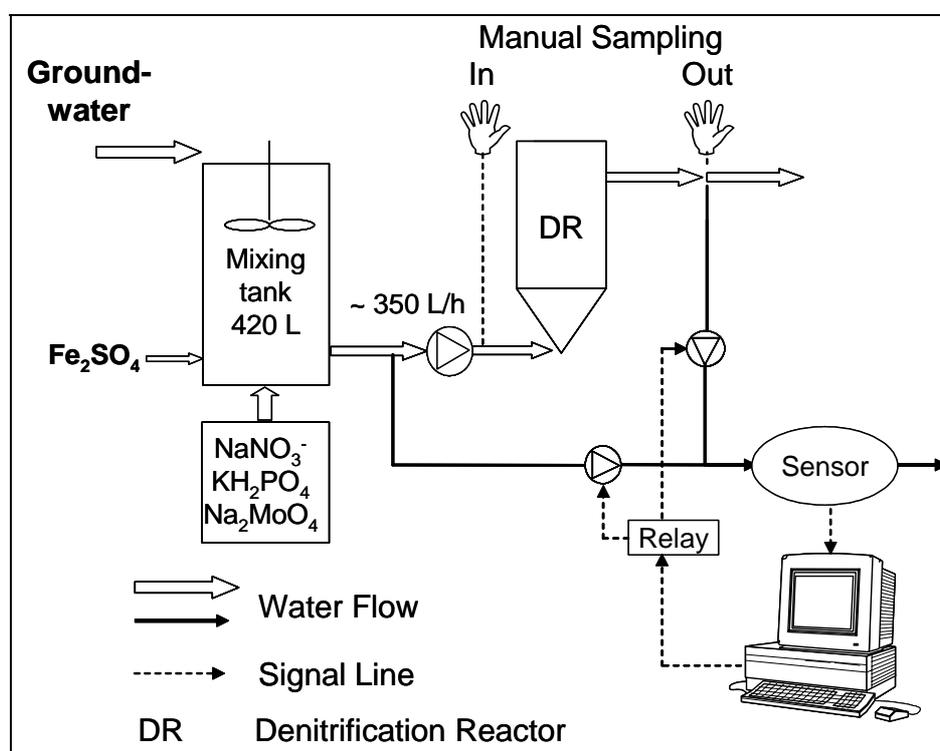

Fig. 1: Reactor configuration and data acquisition system

RESULTS AND DISCUSSION
Aim

For monitoring a denitrification system in drinking water treatment an ideal sensor system should be able to indicate the essential parameters nitrate and nitrite securely and rapidly to allow a decision to the operator. Classic photometric on-line sensors cannot distinguish between nitrate and nitrite, the value produced is normally a sum of both parameters (NO_3^-N + NO_2^--N). With the multi-wavelength instrument examined a spectrum is acquired, which - on principle - allows differentiating between these two species.

Additional attractive parameters are DOC (TOC) and turbidity for the evaluation of the water quality. Therefore values given by the sensor were also analyzed in the lab and compared.

Nitrate

For this parameter we could observe a quite good conformity in the trend of lab and sensor values after the change of software parameters ("global calibration" corresponding to the actual type of application "drinking water", provided by the manufacturer) at day 9 (fig. 2). This resulted in a better fit of the nitrate concentrations with presence of nitrite. On the other hand it seems that the sensor signals showed a higher noise than before
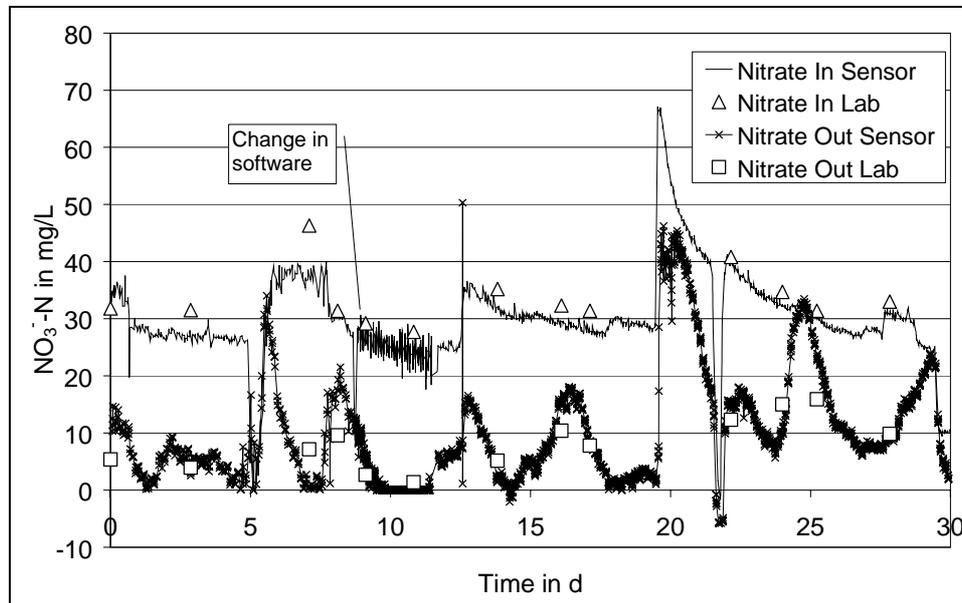

Fig. 2: Comparison of Nitrate concentrations monitored by Sensor and lab-analysis.

Nitrite

In the first 9 d sensor and lab concentrations were quite different Therefore the software parameters were changed (see above). After this change the analytical concentrations fitted better to the sensor values (fig. 3), but - as for the nitrate concentrations - the noise factor increased. The peaks for the nitrite concentrations especially in the influent of the reactor at day 20 and 25 are probably ghost peaks, since there is no evidence for a nitrite contamination of the groundwater used. Another point is the very poor correlation of sensor and lab values in the (local) calibration curve, which consists of influent and effluent values (fig. 4). We suppose interferences of nitrite with nitrate concentrations. This has to be proofed by further monitoring as the relation of nitrate and nitrite changes with time. It is difficult to cover these processes both by manual sampling and online monitoring. In addition, the actual concentrations of nitrate and nitrite are not very common in typical drinking water applications – using a shorter light beam path could possibly lead to better results in the case of these high concentrations. This should be validated by further monitoring, supported by the manufacturer.
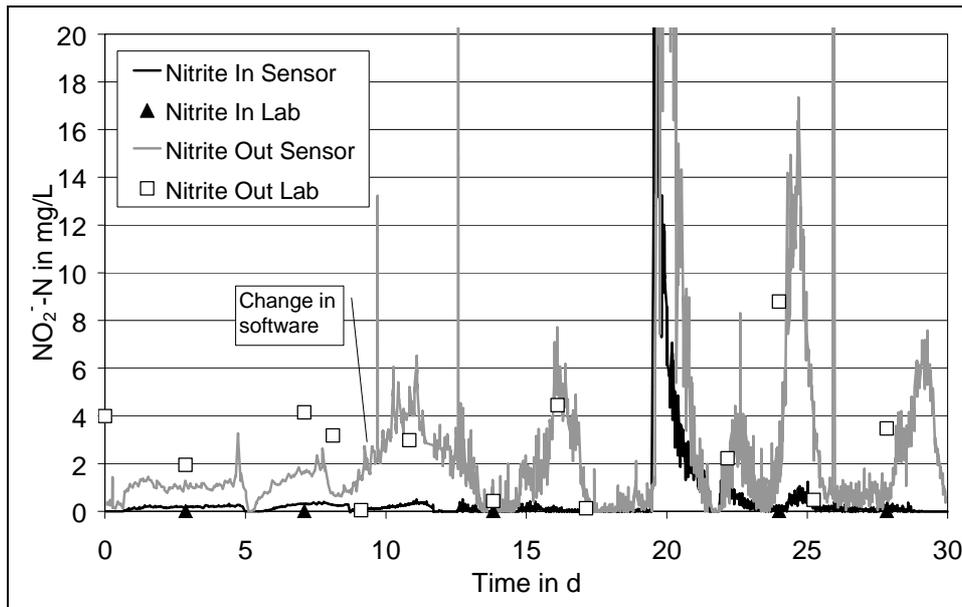
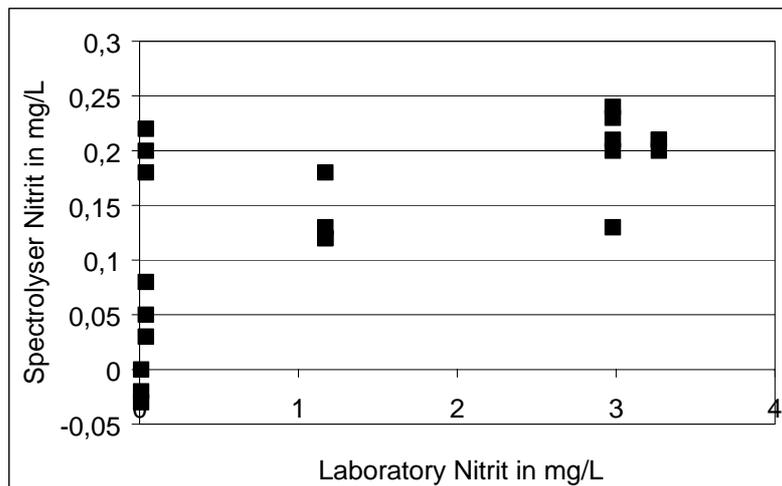Fig. 3: Comparison of Nitrite concentrations monitored by Sensor and lab-analysis.

Fig. 4: Local calibration line for nitrite: laboratory versus sensor-values.

DOC

The data-basis for DOC was yet smaller than for nitrate and nitrite concentrations. Fig. 5 gives an impression of the difficulties in interpreting DOC signals of the sensors. The correlation between the laboratory's results and the readings is not reliable, especially in the inlet. The source of error could not be discovered so far – as the DOC is relatively low and the flow through the bypass is alternating (inlet / outlet). The goodness of the sampling procedure has yet to be analyzed in more detail.
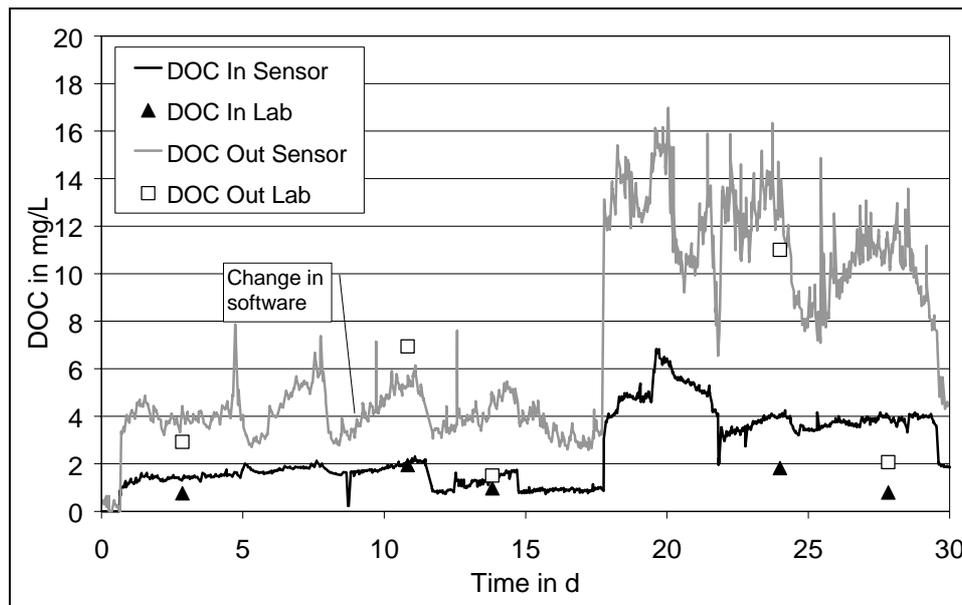
Fig. 5: Comparison of DOC concentrations monitored by Sensor and lab-analysis.

CONCLUSIONS

For monitoring a denitrification reactor the accuracy of the sensor signals is not as important as the reliability. Based on this assumption we conclude that nitrate measurement with the system presented can help to survey a denitrification system. A trend can be recognized, but the nitrite measurement as part of the sensor evaluation is not yet relevant up to a desirable level. Further measurements using a smaller path length shall proof the possibility of online nitrite monitoring. For DOC concentrations the data basis is too low.

It is evident, that further work has yet to be done to fit sensor signals to real conditions. These special conditions of a denitrification reactor and the fact that we used only one sensor to check the influent and effluent, may also play an important role in this context. From a practical point of view our impression as user is that a lot of work has yet to be done to fit the system for this very application.

ACKNOWLEDGEMENT

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