Management of sensible water uses with the help of innovative sensor technology - Part 2: Testfilter results

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Abstract
The LIFE99 project ENV/A/000403 had the objective to develop and test an early warning system. The underlying design concepts have been described in part 1 of this report (Fleischmann et al., 2002). The second part deals with results from the testfilter plant, with operational experience and possible failures of such devices. The disturbances induced by fluctuating surface water quality and their effect on testfilter effluent is outlined. The original concept to operate a hybrid system serving as toxicity detector (fixed bed respirometer) as well as predictor for the water quality of the bankside wells showed unsatisfactory results regarding toxicity. Alternative constructions are proposed. Some considerations about the selection of measurement devices for not standardised monitoring are given and illustrated with examples of spectrometric measurements.

Keywords
Testfilter, toxicity, bankside filtration, drinking water, sensors, spectrometry

INTRODUCTION

There is an abundance of different ways to design and operate testfilters. Usually they are operated either as a closed loop system for a certain period with one sample (several days) or as a flow through system with average retention times between several hours and days (Maelzer, 1993). Combination of different operating principles is just as usual as various filter materials (sand, pumice, GAC...). Sontheimer (1988 and 1991) generally defined Testfilters as a mean to assess the effectivity of biodegradation in a fixed bed system. However, the basic assumption is that the biodegradation processes within the testfilter and in the infiltration zone (from river to the well) are similar.

For bankside filtration alarm systems it is usual to combine groundwater transport with degradation (adsorption, biodegradation..) models. Testfilter experiments are used to derive substance specific parameters for these models (Schulte et al., 2000, and Maelzer et al. 2000). In case of transient pollution events the models are used to predict whether the peak loads will affect the well water quality.

TESTFILTER DESIGN CONSIDERATIONS

The approach of the Vienna Waterworks was slightly different by relying predominantly on real time measurements. Already Sontheimer (1991) recommended to use a continuous SAC 254 measurement to monitor the elimination of organic carbon in the testfilter. A further improvement of this concept was achieved by monitoring not only SAC 254 but the entire UV/VIS Spectrum in-line and to add electrochemical parameters (oxygen, pH, ...). This parameter set was recorded at several points along the testfilter. As a result the following information was available continuously:

- Organic carbon concentration and degradation profile along the flowpath
  - quantitative by the SAC – TOC relationship
  - qualitative by the specific oxygen consumption (mg O_2 per mg DOC)
- turbidity load and elimination efficiency

This set of parameters results in a detailed picture of the processes along the flowpath and over time. In order to assess and increase the reliability of the results two parallel plants where operated and monitored in the same way. The deviations between the two parallel plants describe the precision of the results.

Figure 1 shows a sketch of the testfilter plant and the sampling system. Multiple sample streams are abstracted continuously from the process and alternatingly diverted to a vessel. All sensors are located in this vessel ("Messbox" in Figure 1) where the control system records and evaluates the signals continuously. After stabilisation of the respective signal the control system stores the results and switches over to the next sample. The system was designed in this way in order to guarantee equal conditions for all samples and to achieve comparable and highly precise results from the sensors. The sampling system has the task to bring multiple sample streams to the vessel, without influencing the flow regime within the testfilter columns.

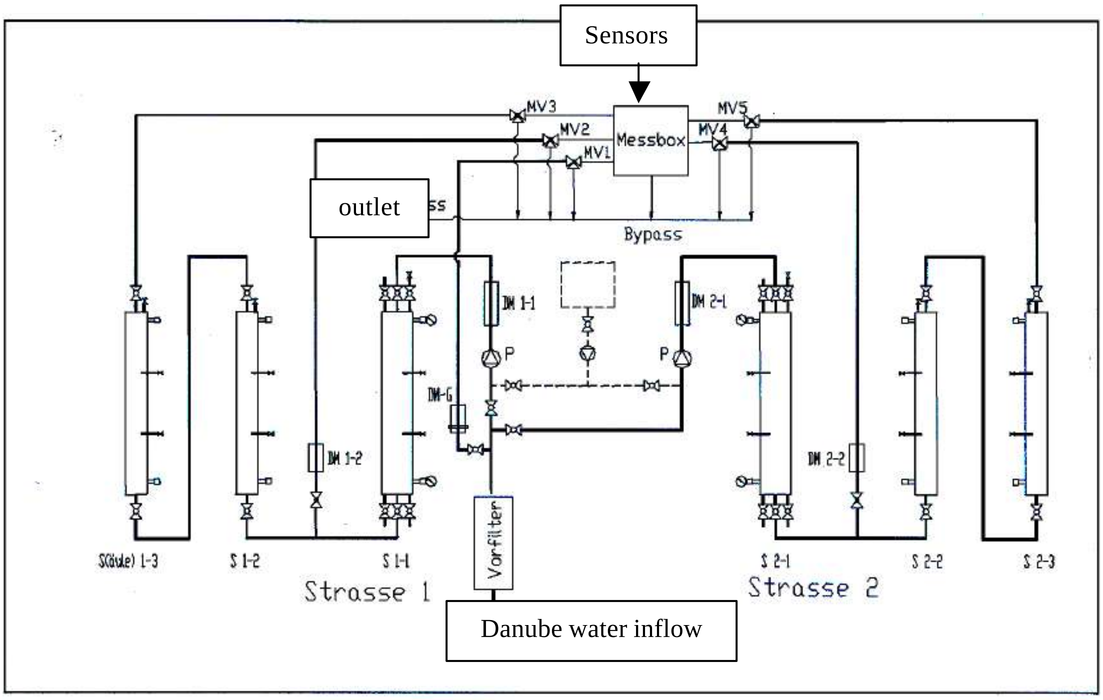

Figure 1: Scheme of the two parallel testfilter plants. Each plant consists of three columns in series.

The transferability of testfilter results from one location to another is poor. Therefore the behaviour has to be analysed for every individual plant. In order to receive reproducible results first experiments concern influencing factors that can be controlled, like flow, hydraulics, load and temperature. A report on these experiments is given in Fleischmann et al. (2001).

Other important factors like raw water quality can not be controlled, nevertheless it is necessary to differentiate between regular operation and unusual conditions in order to define alarm levels. The operator has to rely on experience. With increasing time of operation these alarm levels and the corresponding data evaluation can be refined. Figure 2 shows by means of UV spectra the effect of two periods of unfavourable river water quality and their effect on the water quality at the outlet of the testfilter plant. Figure 3 displays a simplified view of the same event in order to show the consequence for the testfilter. Although elevated turbidity values in the Danube appear only for a limited period of approximately 9 days, the effect on dissolved organic carbon in the Danube and consequently on the testfilter outlet are lasting for about 1 month.

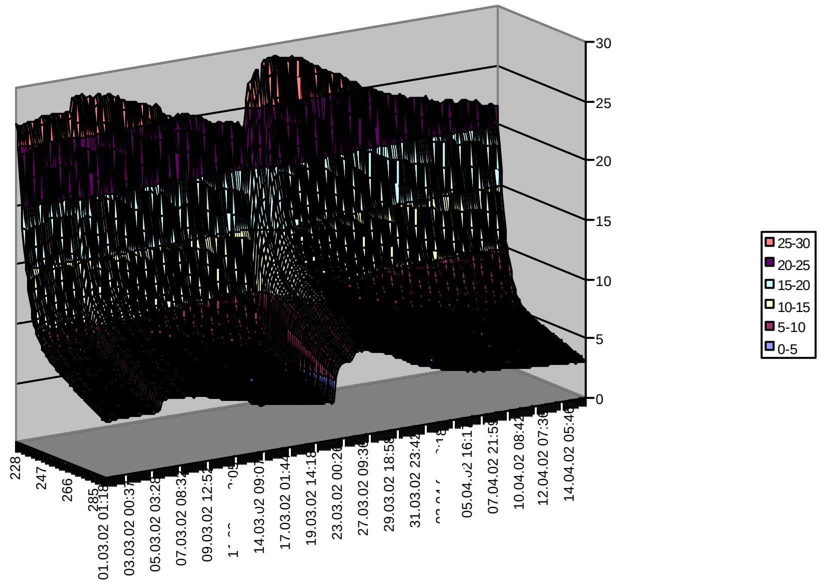

Figure 2: 3-dimensional view of UV spectra over time. The spectra were recorded at the outlet of the testfilter plant. Two periods of heavy rainfall led to elevated concentrations at the testfilter outlet (indicated by the white arrows).

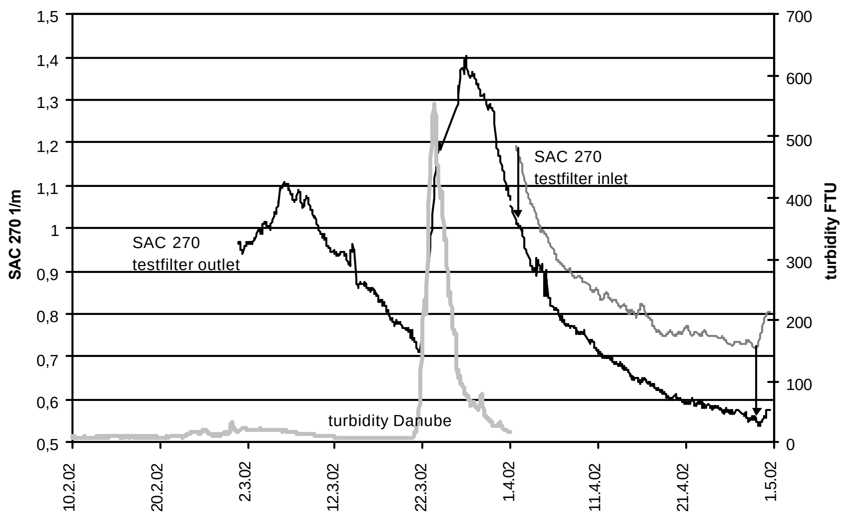

Figure 3: Time series of SAC 270 for the in- and outlet of the testfilter plant. The corresponding turbidity values of the Danube show the reason for the poor effluent quality of the testfilter. The arrows in the right part of the graph indicate that the absolute elimination efficiency of the testfilter has not changed.

TOCXICITY EXPERIMENTS

Still certain cases of disastrous contamination will (hopefully) not take place during this learning period. These cases can be covered by experiments with selected toxic substances. It is the objective to learn the response of the biofilter even for very unfrequent events.

The results of such an experiment are given in figure 4. A toxic substance ($C_6H_5NO_2$ - nitrobenzene) was added to the inflow of one of the two biofilters. Disturbances of the degradation process or any other effect will simply appear as difference (e.g. oxygen consumption) between the two testfilter plants.

Nitrobenzene has a high solubility in water, is highly mobile, not easily degradable and shows the following toxicity characteristics (Koch and Rauner, 1989):

LD50: (oral, rat):	640mg/kg
LD50: (dermal, rat):	2100mg/kg
EC50: Daphnia magna	27mg/L/48h
EC5: Pseudomonas putida	7mg/L

The nitrobenzene solution contained 100mg/L $C_6H_5NO_2$ and 1.5 g/L KCl was added as a salt tracer in order to represent the transport process. The dosage of 100 L of this solution took 3 hours. At the effluent of the first column (after 3 m) peak concentrations reached up to 77.4 mg/L and at the effluent of the entire plant (after 9 m) 67 mg/L.

An inhibition could not be produced by this experiment and the result is consistent with a number of others. Neither during the time of high concentrations nor afterwards a reduced oxygen consumption could be registered, in contrary, the contaminated plant showed significantly higher oxygen consumptions for about 20 hours.

In Figure 4 the measurements at the outlet of the first column are displayed. The reference measurements of the oxygen concentration are represented by circles for the contaminated plant and by triangles for the not contaminated plant. The conductivity measurements represent the transport process of a conservative tracer.

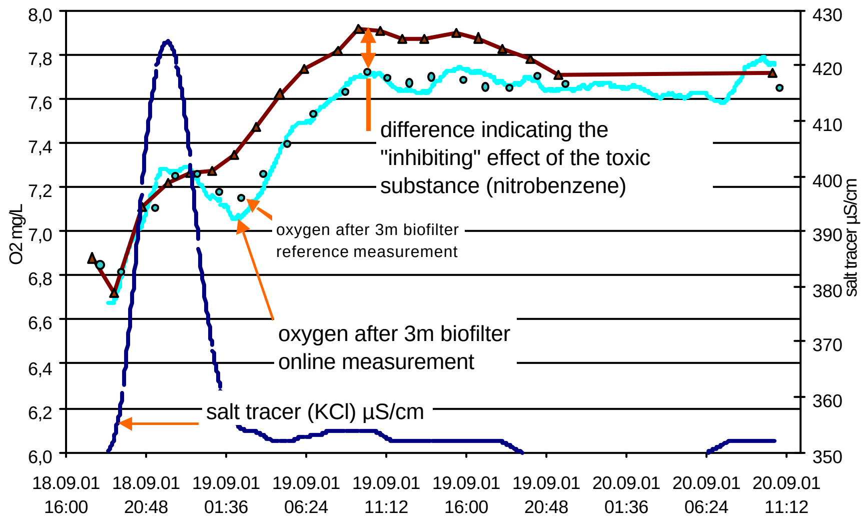

Figure 4: The difference of the oxygen concentrations shows the effect of nitrobenzene on the degradation activity. The conductivity values ("salt tracer") show the dispersion of a 3h dosage of KCl as tracer. The time lag between the tracer and the respiratory effect (19.9.01 00:00 – 20:00) of nitrobenzene suggests that the tracer and the contaminant are subject to different transport Phenomena.

The precision of the oxygen measurement can be assessed by comparing the reference measurements (circles) with the online measurement (light grey line). Differences beyond 0.1 mg are considered to significantly indicate an inhibition. The usual oxygen consumption in the testfilter plant is between 2-5 mg/L. In other words, under optimal conditions this type of experiment can identify an inhibition of 2 %, but it is more realistic to calculate 10 % inhibition as lower limit.

From the toxicity data it could be expected to produce a significant effect on the activity of the microorganisms. But on the contrary the results indicate that the toxic substance was adsorbed and partly degraded. The most probable reason is that the attached microoganisms are unsusceptible for transient toxic shock loads.

This results in two conclusions; on the one hand it underlines the stability of the riverbank filtration process, but on the other hand it must be said, that even peak loads of 80 mg/L nitrobenzene will pass the testfilter without being detected.

Alarm systems are confronted with a variety of phenomena and substances and will never be able to cover all possible hazards. Nevertheless the performance will improve with the number of different

parameters. A combination of measurement techniques with different selectivities and sensitivities is able to detect a greater number of undesired substances or conditions.
As an example for this concept Figure 5 shows the results of the UV/VIS inline measurements for the above mentioned experiment. The graph displays the absorption spectra recorded at the outlet of the contaminated column 1. It can be seen that the applied concentrations produce a very clear spectral signal. Accompanying calibrations resulted in detection limits between 0.1-0.3 mg/L. In this case the direct measurement of the substance is by far superior to the testfilter performance.

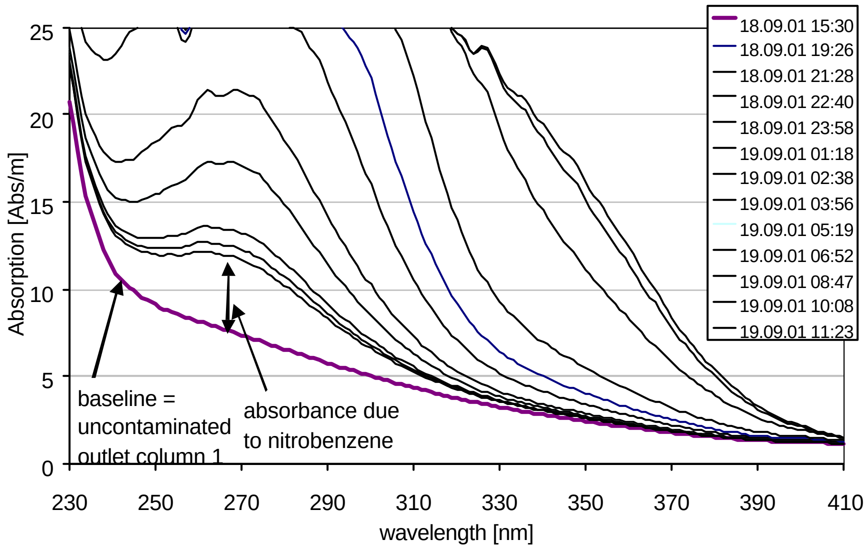

Figure 5: UV spectra recorded during the contamination experiment. Whereas the testfilter could not identify a contamination of this type, the spectrometric sensor would be sensitive enough to detect nitrobenzene down to the sub-mg level.

Possible improvements of the biomonitor (testfilter)

It was the intention of the testfilter design to compromise two different tasks which could be described as follows:

1. "*well water quality prediction*": To imitate the biodegradation along the underground flowpath The objective is to predict the water quality of the bankside wells. For this task a high similarity of testfilter and riverbank filtration is essential.
2. "*toxicity detection*": To detect hazardous or toxic substances in the Danube water, unregarded the effect these substances might have on the riverbank filtration. In this case the sensitivity of the microorganisms in the testfilter has to be higher than in the riverbank aquifer. The objective is to detect potentially harmful substances.

Obviously these two tasks are controversial. On the one hand a stable biodegradation during riverbank filtration and consequently also in the testfilter is desired on the other hand sensible microorgnaisms are necessary for detection of harmful substances.
The concept was based on the assumption that the concentration profile along the flowpath shows an exponential decrease. Figure 6 shows two longitudinal profiles of oxygen concentrations, it underlines that toxic shock loads will mainly affect the initial part of the biofilter and change the usual shape of the degradation profile along the filter. The degradation profile can be registered either by oxygen measurement or substrate concentrations. Thus a number of measurement points along the 9 m flowpath was provided, whereas the first ones where meant to be the "toxicity detector" and the last one (after 9 m filter length) to be the "well water quality predictor".
Nevertheless the results of the toxicity experiments showed limitations of this concept. Especially the "toxicity detection" did not show a satisfying performance in the desired concentration ranges and for the desired substances. Actually the stability of biodegradation with attached heterotrophic biomass, is one of the most striking reasons for the application of the riverbank filtration process,

therefore it is indeed not a good idea to perform toxicity measurements with biofilters. Moreover variations of the water quality at the inlet (organic carbon concentration and composition, daily oxygen fluctuations) result in a number of variations of the degradation process, making it difficult to identify the inhibitions amongst all these fluctuations. For instance Figure 6 shows rising oxygen values due to the superposition of changing inlet concentrations, transport and consumption.

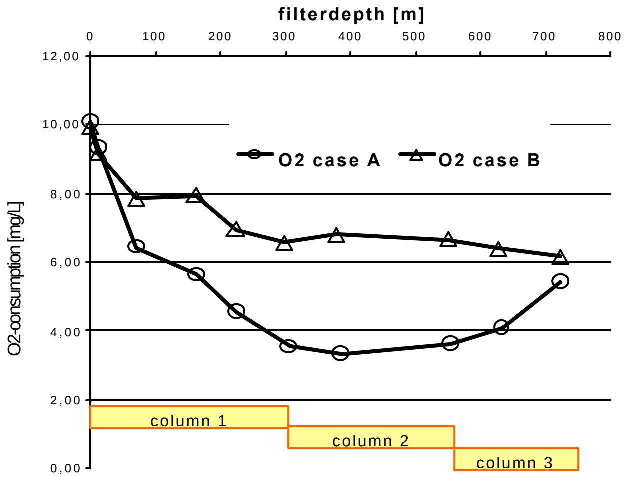

Figure 6: Longitudinal profile of oxygen concentrations in the testfilter.

One possibility to deal with these disturbances is an interpretation with the help of a suitable transport model.
A possible improvement could be achieved by growing more sensitive microorganisms and by eliminating degradation rate changes which are caused by load variations. The concept could be realised by dosing a constant load of ammonia nitrogen at a certain point in the last 2-3 meters of the biofilter. A population of nitrifiers will grow and show constant conversion rates. Nitrifiers are known to be more sensitive to toxic substances and the products, metabolites and effects of nitrification can easily be measured online in terms of nitrate and nitite (UV-spectrum), oxygen consumption and pH. By observing even the intermediate steps via nitrite a detailed picture of disturbances of the nitrification process can be expected.
Another future concept could use suspended instead of attached biomass. The advantage of the "broadband" sensitivity of a mixed culture would remain and the disadvantage "well protected" biofilms could be eliminated. High biomass concentrations are desirable for a fast biomonitor. A membrane labscale bioreactor could cope with these requirements.

CHOICE OF MEASUREMENT TECHNIQUE AND MAINTENANCE

The number of chemicals which might affect the water quality is uncountable and it will be virtually impossible and also not necessary to monitor each compound individually (even if analytical methods existed). There is often considerable information from variables called "surrogates" that are correlated to other variables (e.g. Faecal coliform, conductivity, pH..). Another possibility are aggregate variables that quantify a groups of compounds, based on similar characteristics (AOX, SAC, BOD). Biological variables have aggregate variable characteristics (Niederländer et al. 1996).
In case of not standardised monitoring tasks the selection of the most appropriate measurement techniques / parameters is one of the difficulties. Especially because there is no general consensus about the meaning of equivalence of several measurement methods. Equivalence can be understood in many different ways. The water quality manager will most probably emphasise that the resulting "information" about the observed system has to be equal, whereas a chemist might disregard the observed system and compare the methods solely with chemometric descriptors.

Most of the available sensors are not standardised and the specifications of the instruments can not cover all the details, that might be of importance for a single application. In most cases it will be at least necessary to validate the results and to trace the deviations from reference methods.
In this project the electrochemical probes have been controlled with reference instruments and with standards. In the initial phase more frequently in order to collect sufficient information on the longterm stability etc. The results have been used to define the maintenance requirements of the system. The underlying principle is that the deviations from the true value have to remain smaller than the "relevant margin". The relevant margin can be characterised as the margin in the information that is still relevant to the user, or as the difference between measurement values that still can be interpreted.

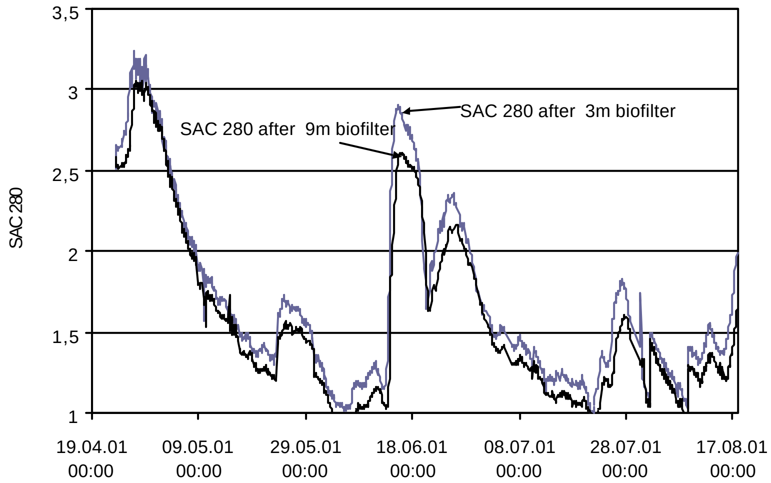

Figure 7: Time series of SAC after 3 m and 9 m of biofiltration. The differences between the lines correspond to a DOC of 0.15 mg/L.

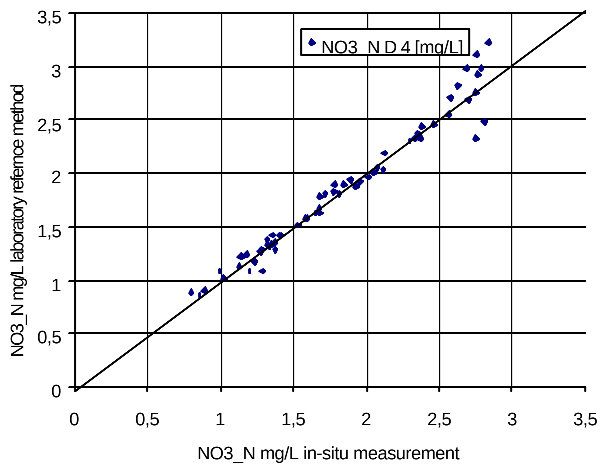

Figure 8: Recovery function for the in situ Nitrate Calibration.

The spectrometric sensor has been controlled with an extensive programme, covering the following aspects:

- Instrument stability
- Fouling of instrument – water interfaces
- Stability / Robustness of the calibration
- Signal quality / precision

The monitoring of the testfilter is a difficult task because organic carbon degradation is very low. The average degradation is 0.5 mg/L DOC. The differences between the sampling sites along the filters could definitely not be measured with standard laboratory DOC analysis based on grab

samples. Averaging multiple analysis is costly and did not sufficiently improve the precision of the whole measurement chain (sampling, transport, analysis). So as a consequence it was impossible to calibrate the spectrometric sensor for DOC, because no reproducible DOC results.
Nevertheless the SAC online measurements produced interpretable results also witout calibration. Even the removal of organic carbon within the last two columns could be detected continuously at any time the two lines in Figure 7 can be discriminated. The average DOC difference between these two sampling points over two years of operation is 0.15 mg/L DOC.
This high precision would be more advantegeous for closed loop testfilter systems, because they do not have to deal with rapidly changing raw water qualities.
For other spectrometric parameters the local calibration prooved to be a practicabel strategy. As an example the recovery function for the Nitrate calibration is displayed in Figure 8.

CONCLUSIONS

The combination of a testfilter with electrochemic and electrooptic sensors and a telemetric network helped to cut down maintenance cost. Due to the sensor measurements the fully automated plant works routinely without sampling and laboratory analysis. Nevertheless it delivers informative results about the biodegradability of the organic substance to the operator. The approach to identify toxic loads showed unsatisfactory results. A modified principle of operation, based on dosage of ammonia nitrogen might help to solve this problem. The underlying data evaluation procedures should be supplemented with a transport model, in order to compensate for varying water qualities at the inlet. The automated monitoring of a testfilter plant proved to be a feasible concept. The principle of local calibration was applied successfully for some parameters but regarding DOC degradation in the Testfilter it was limited by the respective reference method (including the sampling procedure). Other calibrations proved to be relatively robust over several months, nevertheless it is advisable to routinely control the sensors with reference measurements.

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