UV/VIS spectroscopy for the monitoring of testfilters

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Abstract
Testfilters are a means to imitate elimination processes in riverbank filtration. They give evidence about the biodegradability of organic substance in surface waters. Testfilters are used successfully at a couple of waterworks, e.g. on River Rhine and River Elbe, as an early warning system. Disturbances of the elimination process due to substances toxic for the sessile microorganisms can be identified and quantified. The sensitivity of the testfilters depends upon the parameters selected to monitor the organic carbon concentrations. This poster addresses the monitoring of testfilters operated at the River Danube, especially the application of an UV/VIS spectrometer in comparison with standard DOC and TOC analysis.

Keywords
monitoring, surface water treatment, testfilter, UV/VIS spectroscopy.

INTRODUCTION

Within the LIFE99-project "Management of sensible water uses with real-time measurements" (Fleischmann et al., 2001) testfilters are operated at the Danube Island (Vienna, Austria). Testfilters are a model environment to imitate the biological degradation processes taking place during riverbank filtration. This work deals with the monitoring of these testfilters, especially with the application of an UV/VIS spectrometer.

The underground passage from the river to the well can be regarded as the first step of drinking water treatment. Biological degradation and dispersion lead to a very efficient attenuation of shock loads. But this includes, that the concentration changes, which have to be detected in the filtered water, are very little. Therefore a high sensitivity of the monitoring parameters is of paramount importance (e.g. Gimbel and Mälzer, 1987).

Hazardous substance in the raw water can cause disturbances of the biological degradation process, leading to problems in the further treatment steps at the waterworks or even to inferior quality at the point of use. The objective of testfilter plant design and operation is to reach a high similarity between the biological processes in the riverbank and in the testfilter columns (Mälzer et al., 1992). More than 90% of the degradation takes place within the first meters of the underground passage. With the help of testfilters statements about substances expected to pass the bank filtration can be made before they appear and are detectable in the well at the end of the riverbank filtration (the water commonly needs a several weeks to pass the bank filtration).

Testfilters also allow to study the relevance of worst-case scenarios, like a contamination of the river water by oil or other chemicals, just by mixing the contaminants of interest to the feed water. However, if adsorption is the main process for the reduction of a studied substance, testfilters are not the method of choice.

Traditionally monitoring evaluates the water quality on the basis of various parameters measured with grab samples. This strategy suffers, like any other compromise, from several drawbacks. There is a considerable delay between the time of sampling and laboratory analysis, which is relevant for an early warning system, in particular. Moreover there are sampling and sample preparation errors of almost unknown magnitude. Last but not least the costs of sampling have to be taken into account.

UV-absorption at a fixed wavelength (SAC), TOC, DOC and AOX analysis are usually used to monitor water quality. If unusual changes of the organic matter concentration or elimination rate are measured, more detailed laboratory analyses are required. It was the objective of this research to find parameters that are more sensible to the quality changes in the testfilter.

MATERIALS AND METHODS

The testfilter system at the River Danube in Vienna has two parallel filters, TF1 and TF2 respectively (Figure 1). Each testfilter consists of three columns. Samples can be taken after 3 m filter depth (i.e. effluent of the first column named TF1.1 and TF2.1 respectively) and at the effluent after 9 m filter depth (i.e. effluent of the third column named TF1.3 and TF2.3 respectively). The first testfilter is used as a reference system whereas the second testfilter is used for degradation experiments with different hazardous substances (Faber, 2000, and Hackl, 2001).

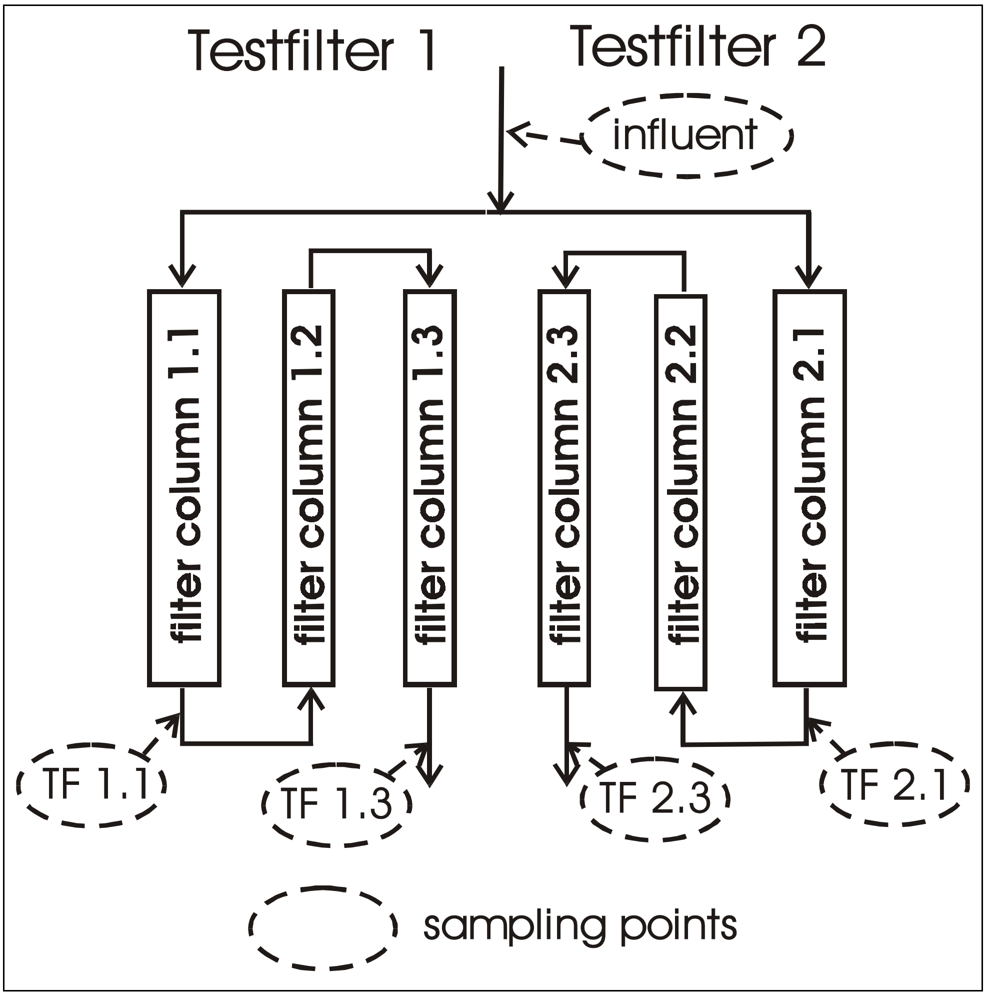

Figure 1. Scheme of the testfilter.

State of the art sensor systems suffer from other deficits, e.g. the limited number of parameters measurable. Therefore the sensor array used for the testfilter system, consists of a novel UV/VIS-range spectral absorption sensor combined with an array of electrochemical sensors (Fleischmann et al., 2001). The most versatile measurement parameter is the UV/VIS absorption spectrum between

200 nm and 750 nm. The optical probe ("spectro::lyser" by s::can Messtechnik GmbH, Vienna) delivers nitrate, organic carbon, colour and turbidity values directly and gives indicative values for aromatic compounds. Moreover the sample matrix is assumed to be characterised by the absorption spectrum as a whole, the so called UV/VIS fingerprint. This approach is based on the assumption that the changes in the spectrum are indicative for certain processes or properties in the system. Based on a training data set discriminating for example usual and unusual sample matrices, sample triggers, alarms or control operations can be set. To measure and evaluate the entire UV/VIS-spectrum improves the quality of statements resulting from testfilter plants compared to conventional sampling and laboratory analysis.

For the compensation of turbidity a mathematical equation was developed which describes the relationship between scattering intensity and wavelength as a function of the particle diameter based on the relationships given by Huber and Frost (1998). The turbidity compensation feature uses the original spectrum and estimates two parameters of the turbidity function. The results of the turbidity compensation showed to be very sensitive to the initial values of these parameters.

RESULTS AND DISCUSSION

TOC and DOC analysis are carried out to characterise the elimination efficiency of the testfilter. Due to the filtration process in the testfilter the measured TOC at the effluent is equal to the DOC. The elimination in the testfilter in terms of TOC is smaller than the accuracy of sampling and TOC analysis. As it can be seen in Figure 2 no difference can be found e.g. between the effluent TOC concentrations of column 1 and column 3 for both testfilters. The measured influent DOC sometimes is even lower than the measured effluent TOC.

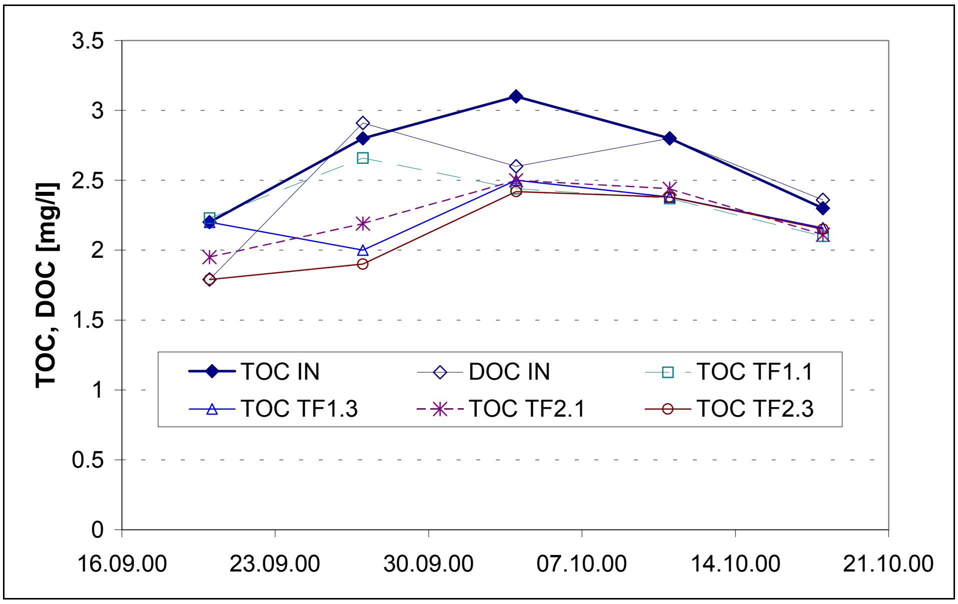

Figure 2. TOC measurements (IN ... influent, TF1.1 ... TF1 effluent column 1, TF1.3 ... TF1 effluent column 3, TF2.1 ... TF2 effluent column 1, TF2.3 ... TF2 effluent column 3).

Figure 3 shows UV/VIS fingerprints for testfilter 1. The turbidity compensated UV/VIS fingerprints are used as a measure for DOC. The linear relationship between DOC and absorbance has been showed by others. Not only the elimination rate of the entire plant but also the difference between column 1 (3 m) and column 3 (9 m) can be clearly seen.

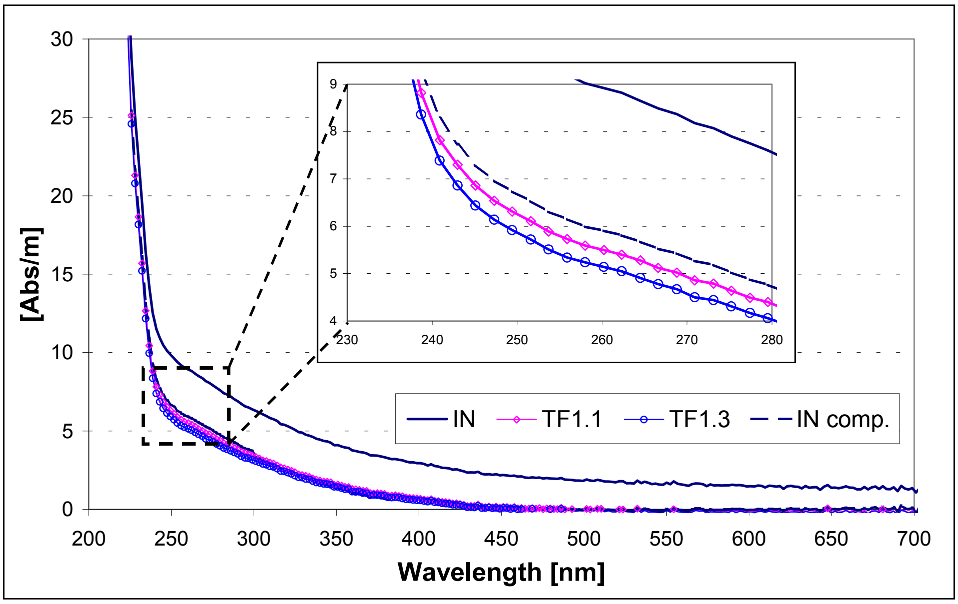

Figure 3. UV/VIS fingerprints for Testfilter 1 (IN ... influent, TF1.1 ... TF1 effluent column 1, TF1.3 ... TF1 effluent column 3, IN ... turbidity compensated influent).

Calibration results for the “spectro::lyser” using data from all measuring points, testfilter and bank filtrate, show good results (Figure 4). The obtained correlation coefficient was 95 %, the mean error 0.07 mg/l). The calibration results for lower concentrations could be improved when using only bank filtrate data (Figure 5).

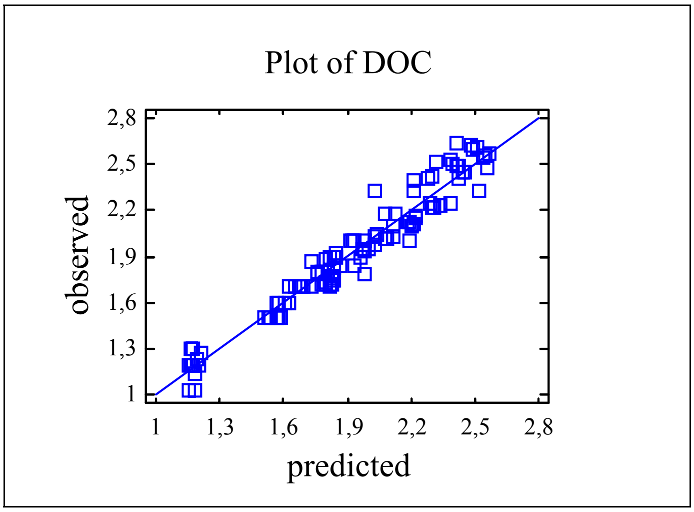

Figure 4. Calibration of the “spectro::lyser” using all testfilter and bank filtration data (r^2=95 %, mean error = 0.07 mg/l).

Using these calibration results the a significant difference between the sample point at the effluent of column 1 and column 3 can be found for both testfilters. Figure 6 shows the Box-and-Whisker plot for the calculated DOC equivalent.

The results show the improved measurement accuracy by using UV/VIS spectroscopy in relation to conventional TOC and DOC analysis. Moreover the spectrometer works automatically in real-time and the measurement frequency does not influence the cost of monitoring.

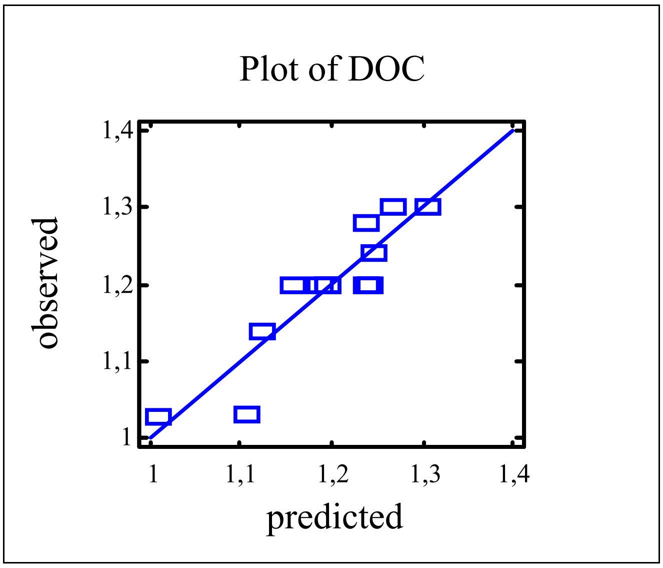

Figure 5. Calibration of the "spectro::lyser" using only bank filtration measurements.

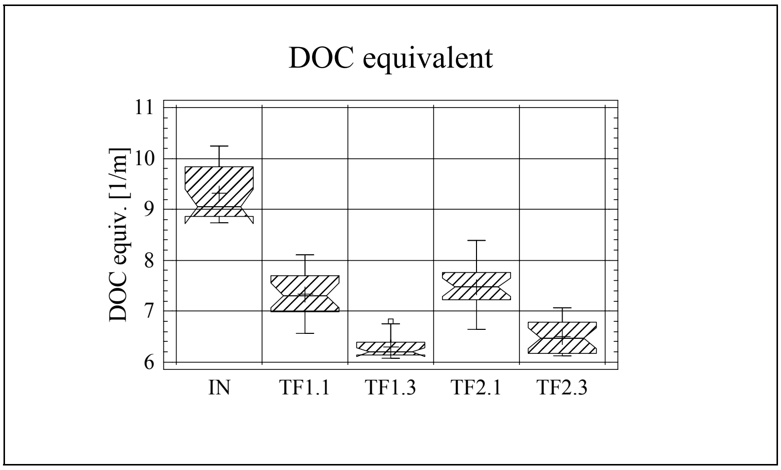

Figure 6. Box-and-Whisker plot for DOC equivalent measurements (IN ... influent, TF1.1 ... TF1 effluent column 1, TF1.3 ... TF1 effluent column 3, TF2.1 ... TF2 effluent column 1, TF2.3 ... TF2 effluent column 3) - *The box encloses the middle 50 percent, where the median is drawn as a vertical line inside the box. The mean is given as a cross. Horizontal lines (whiskers) extend from each end of the box. The lower/upper whisker is drawn from the lower/upper quartile to the smallest/largest value within 1.5 interquartile ranges from the lower/upper quartile. The length of the notch around the median represents a 95 percent confidence interval for the median. The dots represent outliers.*

SUMMARY

The "spectro::lyser" was successfully used for the monitoring of testfilters. Calibration results using turbidity compensated spectra and DOC measurements show a high correlation coefficient. Using UV/VIS spectroscopy a significant difference between the sample point at the effluent of column 1 and 3 can be measured for both testfilters. This was not true for conventional TOC and DOC analysis carried out.

The results show the improved measurement accuracy by using UV/VIS spectroscopy in compared to conventional TOC and DOC analysis. Moreover the spectrometer works automatically in real-time and the measurement frequency does not influence the cost of monitoring.

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