Management of sensible water uses with real-time measurements

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Abstract
For the protection of bankside wells and a groundwater recharge an early warning system had to be developed. The monitoring network design is based on sensor measurements only. For this purpose a new submersible spectrometer has been successfully tested for multi-parameter measurements directly in the medium. The developed system can easily be upgraded with other new sensors. Only calibration and validation data are supplied by conventional grab sampling and laboratory analysis. A conventional test filter improved by on-line monitoring at 5 sampling sites serves as a reference system. The whole system is equipped with remote control and the internet serves as the control centre of the network. All measurement data from all 9 sites are available in real time on the internet.

Keywords
early warning, monitoring network, surveillance, water quality sensors

INTRODUCTION
Almost all water resources show a dynamic behaviour in terms of quality and quantity. The importance of dynamic behaviour is different for every water use and it depends upon the resource of concern. For the management of rainfall runoff in urban areas it will be unavoidable to take the dynamic behaviour into account whereas for drinking water abstraction from a lake it might be of minor importance.

In other words, the potential improvements due to real time process control are defined by the mutual dependence of the natural and the technical system. But the improvements that are realistic for real world applications have to be seen under the existing constraints of measurement technology. These constraints imposed by measurement technology seem to be the bottleneck of process control. On one hand there are technologies that can be seen as automation of traditional sampling and laboratory procedures, i.e. TOC analysers, on the other hand there are new sensing technologies specifically designed to be applied in situ (e.g. photometric probes for Nitrate).

For a first assessment of feasibility a number of criteria can be applied for practicable real time measurement technology (maintenance, precision, trueness, ruggedness,...). At the end of application development from the laboratory to pilot plants there is still a long way to go until a technology can be regarded as state of the art. It is always the performance in real life technical scale applications that decides upon the acceptance.

This work deals with the development of an early warning system for two sensible water uses: Firstly drinking water abstraction from bankside wells and secondly is groundwater recharge with surface water. Therefore a high sensitivity of immediately available monitoring parameters is of paramount importance. It is the objective to find an economically feasible taylor-made monitoring solution.

Driven by the first generation of process analysers many rather optimistic expectations have been reported in the past 10 years but only a very limited number of technologies proved to be
practicable. A “control everything online” strategy seemed to feasible within a reasonable time frame. This ambitious objective could not be reached until now, neither for drinking water, nor for wastewater tasks. Typically the instruments showed good performance under controlled conditions in the laboratory but failed in field applications. Nevertheless the impact of automated measurement on different water management tasks has changed the face of water quality monitoring within the last decade. Due to dramatic progress in electro-optics and semiconductor technology further and even more relevant changes can be expected for the years to come.

Major drawbacks until now were the complicated maintenance and the limited reliability of some instruments. These shortcomings where reinforced by poor data evaluation and lack of experience in quality control and validation of automated measurement technologies (process analytics). It is still difficult and expensive to develop and assess the specifications in terms of long term stability, precision, cross sensitivities of such systems. These chemometric specifications are of general nature and in most cases well known. But it remains a task of case studies to find out which restrictions apply for the specific application. Chemometric figures can give a first indication but the performance under real world conditions remains currently the most important element in the development of new monitoring solutions.

THE MONITORING SYSTEM
The measurement network consists of four monitoring stations that deliver data for a total of 9 sampling sites. The objective is to protect the drinking water wells and the groundwater from unfavourable water quality changes of the river. The potential impacts are numerous due to the large and intensively used catchment area. A selection of the most relevant ones have been done in previous studies.

Each site is monitored by conventional sampling-laboratory methods and by automated measurement devices. Laboratory parameters include TOC, DOC, Nitrate, Chloride, SO₄, PO₄ and SAC 254. On site installations include conventional electrochemical measurements (turbidity, oxygen, pH, ORP, temperature and conductivity) apart from a new electro-optic probe. This probe is basically a submersible UV/VIS spectrometer.

One principle of the field monitoring station design was to avoid any type of automated analysers, sampling, and/or sample preparation (e.g. filtration) but to rely totally on in-situ real time measurements directly in the medium. The limited number of parameters that can be measured with sensors directly in the water is a serious restriction for the system.

Submersible UV/VIS spectrometer
The most versatile measurement device is the spectrometric probe. It measures absorption spectra between 200 nm and 750 nm (in some cases 400 nm is the upper wavelength limit). One basic requirement is long term stability of both the instrument itself and the local installation. Instrument stability is guaranteed by a double beam principle. One light beam serves for the measurement and the other compensates for instrument drifts that might occur due to ageing or temperature changes. The stability of the local arrangement was subject to the developments in the project. A major problem with any type of sensors that are immersed in the medium is biofouling. Bacterial growth on the instrument water interface can lead to undesirable changes of the signal. As there is no general model to predict the influence of biofilms it has to be assessed for every local installation.

A crucial feature for field instruments is their performance with autochthonous samples. Calibration results with pure substances are far from being transferable to the field application. Natural waters,
characterised by a matrix of numerous substances, cause cross sensitivities and the performance in-situ is inferior to the performance under controlled conditions. The possibilities of compensation for cross sensitivities in single/dual wavelength photometers is limited, whereas the aquisition of the entire UV/VIS spectrum allows to compensate for some of these cross sensitivities. In situ validation with reference methods can sometimes reveal the magnitude of measurement errors.

Spectral data are automatically evaluated in order to give evidence about concentrations of Nitrate, Nitrite, several organic carbon surrogates, colour and turbidity and indicative values for e.g. aromatic compounds (Benzene) or substance groups like BTX. Apart from instrumental accuracy detection limits depend before all on the variability of the background matrix. For Nitrate, Nitrite and Benzene they are in the range 100 µg/l. Turbidity is measured down to values of about 0,3 FTU

Moreover the sample matrix is assumed to be characterised by the absorption spectrum as a whole. This parameter could be called a UV/VIS fingerprint. This approach is based on the assumption that the changes in the spectrum are indicative for certain processes or properties of the respective measurement site. Based on a training data set discriminating for example usual and unusual sample matrices, sample triggers, alarms or control operations can be set.

**Testfilters**

The monitoring network includes testfilters as a reference system. In this case study 2 parallel fixed bed filter columns with a depth of 9 m each where used. Continuous measurements are done after 3 m, 6 m and at the outlet of each testfilter (Staubmann et al., 2001).

Testfilters are frequently used as alarm system for bankside filtration wells (e.g. on the River Rhine). Testfilters are a model environment to imitate the biological degradation processes taking place during riverbank filtration (Gimbel and Mälder, 1987). The underground passage from the river to the well can be regarded as the first step of drinking water treatment. 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 in the drinking water well at the end of the riverbank filtration.

The specific novelty in this project is that information about testfilter performance should be collected from on-line measurements only. After an initial calibration phase with the help of laboratory parameters, everyday operation includes on-line measurements and periodic recalibrations only. Detection limits and selectivity of field instrumentation cannot be compared with laboratory trace analysis. Nevertheless for some specific monitoring tasks other considerations like measurement frequency can lead to a superior performance of sensor systems.

**Data Evaluation and Data Transfer**

For early warning systems it is necessary to combine automatic measurement with automatic data evaluation and data transfer. In this measurement network the following elements have been realised:

On site:
- plausibility control and signal conditioning,
- data storage, and
- visualisation.
Telemetry:
- remote control,
- automatic data transfer to a central database, and

Every station is controlled by a custom software, based on the development tool LabView®. The database and the web interface have been realised under LINUX. Plausibility control includes automatic detection of stable/unstable sensor signals in terms of standard deviation and trend as well as limits for the measurement range. Signal conditioning includes analogue and digital filters based on sector-wise and boxcar averaging as well as on polynomial smoothing. Data storage concerns raw and reduced data as well as status reports and user activities. In-situ visualisation depicts graphs of time series with free selection of parameter and time scale.

The web interface is based on the idea of maintenance on demand. The web interface can be regarded as a control centre. The responsible person can assess the proper operation of the system from everywhere and at any desired time. Graphic inspection of the results is done by selecting the parameter, the measurement site and the time scale. In case of irregularities on site it is possible to remotely control the system, to change settings or to check the raw data. Just in case that the problems cannot be settled that way somebody has to visit the measurement station. The desired effect is to reduce maintenance cost due to regular travels to the measurement sites, but without inducing drawbacks on the reliability of the system.

SELECTED TECHNICAL ASPECTS

Testfilter tracer experiments with artificial tracers
The first step of interpretation uses the measurements at the outlet of the last columns only. These values and their changes over time are tested whether they are in the expected range. Most changes at the outlet are not due to disturbance of the degradation process but due to changing quality of the feed water. Therefore the second step of interpretation evaluates elimination rates, oxygen consumption and other changes from the inlet to the outlet. For this purpose a transfer function that describes the hydraulic properties of the columns is needed.

Fixed bed columns filled with a standard filter material usually have very clear hydraulic characteristics (Figure 1). During operation these characteristics can change due to bacterial growth, and due to inhomogenities of the filter material. The model should then be used to transform the time series at the inlet into time series at the outlet. In this step every substance is regarded to behave like a conservative tracer (Figure 2). The elimination rates calculated during normal operation should then be compensated for changing feed water qualities, like e.g. diurnal oxygen fluctuations.

KCl was used as tracer and measured with conductivity sensors. Prior and after the tracer experiment the measurement method was calibrated with KCl standard addition to the natural feed water. The confidence limits of these two calibrations were used to produce the confidence limits for the experimental results (Figure 1). For every tracer experiment a KCl mass balance was calculated (Table 1).
Figure 1: Results of one tracer experiment with 17L/h in the first column and 10 L/h for the third column (right ordinate). The strong line with two peaks shows the KCl load in mg/min (left ordinate) and the respective confidence limits.

Figure 2: Comparison of measured tracer load in column 1 with calculations from a simple dispersion model fitted to the experimental data.

**Testfilter mean residence time with natural tracers**
Experiments with artificial tracers are time consuming and cannot be done during everyday operation of the plant. Therefore it was necessary to find an operational parameter, that assesses the mean residence time during normal operation. Cross correlation of inlet and outlet time series showed a sufficient accuracy under certain conditions.
Table 1. Comparison of the measured and calculated tracer loads for different experiments.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Tracer load measured (mg)</th>
<th>Tracer load simulated (mg)</th>
<th>Difference (%)</th>
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<tbody>
<tr>
<td></td>
<td>Testfilter 1</td>
<td>Testfilter 2</td>
<td>Testfilter 1</td>
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<tr>
<td>1</td>
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<td>18.2</td>
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Figure 3 shows the result of cross correlation inlet and outlet oxygen concentrations. The mean residence time in this case is about 7.5 h. The most important condition for good results of this method is that there are fluctuations of the parameter at the inlet and that they are still significant at the outlet. Otherwise misleading results can be produced.

Parameter development
Single wavelength photometry is well known in water quality monitoring, both under laboratory and under field conditions. Many methods have been reported and are state of the art. Single wavelength photometry measures single parameters and in natural waters it suffers often from cross sensitivities, because the sample matrix changes. An improvement could be expected from the submersible spectrometer, that acquires the entire UV/VIS spectrum instead of single wavelengths. It allows for multiparameter measurement and is less prone to cross-sensitivities. The new device is one of the cornerstones within this work. But field conditions are different from laboratory conditions and therefore also new ways of compensation and calibration had to be developed.

The most important influence on spectra is light scattering due to suspended matter (Huber and Frost, 1998). The scattered light will not reach the detector and causes light losses that do not
correlate with the parameters of concern. Within this work a new method to compensate for this influences has been validated. The method is based on the assumption, that there exists a wavelength region where only the effect of suspended matter can be measured. This region is between 500 nm and 750 nm. The algorithm tries to identify the optical properties of suspended matter and should substitute filtration. These optical properties depend among others on particle size, refraction index, surface properties and on concentration. Once these properties are measured the effect of suspended matter can be calculated for every other wavelength.

Validation has been done by measuring the UV/VIS spectrum of the unfiltered and filtered sample. The difference was considered to be the absorption (scattering) spectrum of suspended matter. This measured spectrum was compared with the one calculated by the algorithm. The results showed that the differences depend on the wavelength and will usually be approx. 5 % - 10 % (Figure 4).

There is a remarkable difference between the measured and the theoretical spectra of suspended matter (in Figure 4 the dotted line shows the expected shape). Obviously some of the absorbing dissolved substances remain attached on the filter. The resulting spectrum of suspended matter shows a spectral shape that cannot be explained with light scattering. In case this phenomenon can be verified it would have major consequences on every analysis of filtered samples.

Figure 4: Difference between measured and calculated spectra of suspended matter. The shoulder in the wavelength region between 250 nm – 340 nm is due to errors induced by the filtration process itself. Theoretically spectra of suspended matter do not show any spectral shape but exponential increase with shorter wavelengths.

Calibrations of spectral parameters can give very precise results for a single sampling site, but spectral parameters of a more general nature was the objective of this work. Figure 5 shows the recovery function of a spectral surrogate parameter, that is valid for all the sampling sites within the project. This includes the unfiltered river water as well as the bankside filtrate.
Figure 5: Recovery function for TOC and spectral measurement of a surrogate parameter.

**SUMMARY**

Although there were great developments over the last years, process analysers that fulfil all the criteria for on-line water quality management are still available only for a small number of parameters. Nevertheless, the described early-warning system indicates that using intelligent data combination, interpretation and visualisation much better information on water quality can be produced by measuring these few parameters on-line in comparison with grab sampling and laboratory analysis. The system relies on on-line measurement of substances in water (UV/VIS spectroscopy) as well as on the detection of changes in water quality due to biological effects (e.g. change in O₂-consumption). The sensitivities of such a system may change from case to case and the time and effort needed for the evaluation is one drawback. At the portrayed installation
experiments to describe the sensitivity are still going on and will hopefully reduce this effort for further systems.

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