Adaptation of a new online probe for qualitative measurement to combined sewer systems

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Abstract

Qualitative measurements in combined sewer systems lead to high demands on the measurement equipment. This paper describes the application of a newly developed measuring device for continuous measurements in combined sewer systems. First results with a prototype tested in municipal waste water show a very good representation and correlation of the physical parameters measured by the online-probe and the chemical analysis of samples in the laboratory. Measurements in industrial waste water with varying colors and concentrations made it necessary to develop a specialized calibration model. Finally, the paper describes an improved version of the measuring device, that was developed during a research project. In the future, this device will be used for continuous measurements of the parameters COD, SS and SAC in a stormwater overflow.

Introduction

Continuous measurements in sewer systems are a special challenge for the implementation of measurement equipment and it's operators. Until recently, they were limited to physical parameters like water level, temperature, and flow. For control purposes, however, bio-chemical parameters are measured over a limited period of time. For these measurements, bottle sampling devices with subsequent chemical analysis are commonly used. Nevertheless, bottle sampling devices are unfit to supply continuous measurements for the purpose of online-monitoring and load-dependent control of combined sewer systems.

Probes in combined sewer systems allow to directly record changes in the composition of the waste water and to record data for online control purposes. Bogaczyk, D. (2000) divided measurement systems into continuous and discontinuous systems. For discontinuous measurements, a separate flow was split from the combined sewer system and pumped through a bypass into a black box (i.e. a small storage tank). The latter contained the probes. The time needed to fill and empty the black box determined the time needed for a measurement-cycle. The signal from the probe showed a time-lag, because some time was passing between the extraction of the sample from the sewer and the subsequent measurement with a probe. For continuous measurements, the probe is located directly in the sewer. Under these conditions the probe was sending a dense signal with minimal time-lag.
Weilandt, M., et. al. (2001) described continuous measurements with a SAC-probe in combined sewer systems. Direct measurements with the probe in the sewer led very to strong ragging of the probe. An accurate operation was not warranted, because the measuring window was blocked with toilet paper and sanitary products. The ragging resulted in erroneous data. Häck, M., et. al. (2001) tested a SAC-probe and a turbidity-probe directly in a combined sewer system. Along side he tested a black box system with SAC-probe which supplied differing data. On the suction head ragging occurred and solids settled in the black box. These measuring methods were unsuitable for continuous measurements. Moreover, it was essential to use a separate probe for every parameter. This proved to be a further problem.

In contrast, with a new multivariable spectrometer probe, the spectro::lyser manufactured by s::can - liquid monitoring networks, Vienna, Austria, it is possible to measure several parameters such as COD, SS, TOC, and NO3 simultaneously with a single probe. Comparative measurements of wastewater in the branch of wastewater treatment plants from independent laboratories showed that this a suitable probe to measure water quality (s::can (2001)). The correlation between laboratory COD and the instrument measurement COD was good ($r = 0.75 \ldots r = 0.90$). A very good correlation was found between the solids and the s::can extinction parameters with $r = 0.95 \ldots r = 0.99$.

In the present project we have tested the suitability of the probe for measurements in combined sewer systems with municipal and industrial wastewater as well as with stormwater. Moreover we have developed a new probe system requiring low-maintenance and adapted it for continuous measurements in combined sewer systems.

**Probe requirements**

A continuous measurement system in a combined sewer system must accommodate the highly different conditions during dry-weather and storm-weather flow as well as the inhomogenity of the waste water. Therefore, measurements with online probes require:

- A robust, waterproof, and corrosion-resistant probe-casing with an automatically cleaned measuring aperture (wiper or compressed air)
- Solid support of the probe in the sewer
- A well accessible sampling point in the sewer
- Measurement in the center of the stream
- Spark-proof, uninterrupted power supply and data transfer.

The multivariable spectrometer probe has for instance the following advantages compared to simple process photometers (s::can (2001)):

- High precision, selectivity and reproducibility
- Calibration of various substance groups
- Lower cross-sensitivity on turbidity and coloration
- High measurement dynamics with a great measuring range
- Long-term stability with dual-stream measurement
- Nearly no maintenance necessary due to because of window-cleaning using pressured water or compressed air.
For measurements in combined sewer systems other specific properties are required in addition:

- Regular window-cleaning to prevent drift in consequence of a color film, fat coating or biological surface growth
- Explosion protection for use in the sewer atmosphere
- Dynamic collection of stormwater occurrences with very short measuring intervals
- Detection, identification and monitoring of indirect inlets in dry and rain weather conditions

The location of the test point

The location of the test point is very important for the representation of measurements according to german standard DIN 38402-11 (1995). The measurement takes place directly at the inlet and outlet of the combined sewer overflow (CSO) in the sewer system as well as at the overflow. The sampling point (ATV-FA 1.2 (1990)) is in a zone of good mixture and approximately 10 to 30 cm under the surface. Other investigations from Wöhrle, C., et. al. (1991) acknowledged these statements. Particularly measurements directly at the inlet resulted in six fold higher concentrations.

The wide range of measurements experienced in combined sewer systems result in the following test point requirements:

- Measurements in outlets without backwater to prevent ragging
- Measurements in fully stirred streams yet with flows as laminar as possible with little turbulence to prevent air bubbles in the measuring window
- Easy and safe access to the test point and the measuring equipment during day and night time even in busy street conditions.
- Simple maintenance of the measuring equipment in all weather conditions.
- Compliance with health and safety regulations (for instance good ventilation of the sewer system).

The prototype

For the research project in the town of Burscheid, Germany, the authors developed a new measuring device with an integrated spectrometer probe on a boat-like pontoon. The floating measuring device takes continuous measurements in the sewer without being influenced by the varying water levels. A rope secures the power supply and the data transfer line.

Figure 1 shows the floating measuring pontoon with the integrated multivariable spectrometer probe. In order to adapt to various water levels the casing consists of a package of carbon-reinforced glass-fibre material. The pontoon features at its front a fore of styrofoam. This is to prevent ragging and sedimentation settlement. The probe has been placed in a pipe in the pontoon's keel. The submerged depth was only 8 cm measured from the prototype's window up to the water surface. A cable and a tube responsible for leading the compressed air out of the pontoon are connected from the stern to the control box.
The points of measurement

Measurements with the prototype took place in the town of Burscheid at two different inlets and runtimes. This was done during rain weather overflow conditions in front of the overflow sill from CSO “Luisental”. These two waste waters had different characteristics. There was only municipal waste water in the inlet no. 2. However in the inlet no. 1 besides municipal waste water, industrial waste water was also found. This was due to intermittent discharges from a dyeing factory into the sewage system of Burscheid. As a result, strong fluctuations of color and concentrations were occurred with particulate lather.

Figure 2 shows the installation of the measuring pontoon in the rectangular inlet channel no. 2 from CSO. Inlet channel no. 2 carried municipal waste water. In dry weather conditions the water level was approximately 15 cm due to small backwater flows. The pontoon was fixed on a stainless steel guy, so that the measurement equipment could be adapted to varying flow situations. At the rear of the pontoon samples were taken with a 10 liter-bucket. From these 10 liters, 1 liter-samples were taken for laboratory analysis. Besides other parameters such as COD and SS, SAC was determined in order to compare the measurements of the spectrometer with laboratory analysis.
An alternative application of the probe in the future is its installation on top of a weir in combined sewer overflows. The probe is to be installed perpendicularly to the flow direction, with its measuring window parallel to the overflow. The rope and the cable are in a ductwork to prevent sedimentation problems and ragging.

**First results**

First results with municipal wastewater show a very good correlation with conventional sampling devices, even if only global values are used to calibrate the probe. The precision of the measurement distinctly improved with a localized calibration. In industrial wastewater, a fairly complex spectral calibration is necessary to solve problems caused by the dynamically changing sample-matrix.

Figure 3 shows the correlation between laboratory COD and s::can surrogated COD for municipal waste water in dry weather. The diagram shows, that the s::can-probe provides very good results for municipal waste water with a global calibration ex factory. The results are different for measurements in colored industrial waste water.
Faulty correlations were only noticed during a few measurements of municipal waste water and overflows. The sources of error were possibly:

- waste water flow perpendicular to the measuring window
- air remaining in the measured window after the cleaning with compressed air had taken place
- waste water inhomogenities during the sampling probe.

In colored industrial waste water, faulty measurement results were caused by the formation of a colored coating on the measuring window. However, this problem could be solved by reducing the cleaning intervals.

**Global and local calibration**

The sensor provides a global calibration for the parameters of concern. A global calibration expresses for measurement sites of a specific type (e.g. “stormwater overflow”, “primary clarified municipal wastewater”, “raw municipal wastewater”) the average properties. Recalibration with local reference samples can result in a superior performance (trueness and precision) for quantitative measurements. Especially when the water matrix is unique at the respective measurement location a local calibration is unavoidable, like it was in this case where a mixture of industrial, municipal wastewater and stormwater runoff where of concern.
Hence, a good calibration function is an essential part of the measurement method, as it will reveal the feasibility as well as the quality of the in-situ measurements. Local Calibration is based on reference grab samples analyzed for the parameters of interest.

Some rules are essential for local calibration:
- Validated reference methods for laboratory analysis
- Minimized errors induced by sampling and sample storage
- Identity between sampled liquid and liquid measured in-situ
- Reference samples cover the entire measurement range and are equally distributed over this range
- Reference samples cover all types of matrix compositions at site
- Randomized sampling in order to avoid correlation of subsequent samples

The most important reasons for a local calibration are:
- Usually water samples show a complicated matrix of organic and inorganic substances. Some of these substances are target substances that should be quantified, others are considered to be a background matrix. The validated ‘local’ calibration function optimizes background signal identification and compensation for the specific matrix at the respective location.
- The in-situ spectrometer is capable of simultaneous multi-parameter measurements. If the spectral shapes of target substances are overlapping they cause cross sensitivities. The validated ‘local’ calibration function minimizes the effect of cross sensitivities that might occur between different target substances

Calculating a validated ‘local’ calibration function is a multi step procedure. Recently the calibration procedure has been implemented in the control terminal software, the only input at the user interface are the results of the reference laboratory measurements. The ‘local’ calibration followed by validation will be subsequently carried out automatically. The calibration algorithm includes the following steps.
<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Method</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Turbidity compensation</td>
<td>Curve fitting</td>
<td>Optional step, a ‘local’ calibration can alternatively be based on raw or compensated spectra</td>
</tr>
<tr>
<td>1</td>
<td>Outlier elimination</td>
<td>Stepwise exclusion of suspected outliers, F- and T-Tests, Cook’s distance</td>
<td>Level of significance and max. number of outliers can be defined</td>
</tr>
<tr>
<td>2</td>
<td>Building the calibration model</td>
<td>PLS (leave one out)</td>
<td>Step 1: minimization of cross validated residuals Step 2: reduction of independent variables</td>
</tr>
<tr>
<td>3</td>
<td>Evaluation of confidence intervals of the calibration function</td>
<td>PLS / leave one out</td>
<td>Cross validation (leave one out) results are used to estimate the goodness of fit and the residuals</td>
</tr>
<tr>
<td>4</td>
<td>Evaluation of calibration function robustness</td>
<td>PLS / Cross validation</td>
<td>A cross validation procedure divides the reduced reference data set randomly into a ‘model’- and ‘validation’- data sets. By comparing the results of all model and all validation data sets a qualitative description of robustness is given</td>
</tr>
</tbody>
</table>

**Problems with the calibration**

An assessment and evaluation of all possible calibration models ("brute force model") is by far not possible (and in most cases not necessary), as there are several simultaneous as well as subsequent multidimensional problems to be solved. Therefore some of the decisions during the calibration procedure follow a straightforward strategy (wavelength selection—how many and which ones) and some others include feedback and repeated calculation (e.g. outlier identification). In general this strategy proved to build rather good calibration models. This is due to the fact that there are usually several solutions of the calibration problem that show similar performance. Due to the high correlation of neighboring wavelengths as well as due to the multitude of absorbances of the matrix, there are many local optima but no outstanding global optimum. However in some very specific cases these rules are of limited value, e.g. because there are some outstanding single influences on the matrix. In these cases a local calibration cannot be done automatically but it requires a careful manual data evaluation.

Even when the above mentioned principal rules for building a local calibration data set are obeyed there are some limitations for the automatic procedure:

- Multiparameter calibration needs some variation of the ratios between the reference parameters, otherwise the specific spectral shape of the substances cannot be identified. This would result in a poor selectivity of the measurement method. As a general rule, high correlations between the dependent variables cause problems for any modeling. In many waste waters one can observe high correlations between the different pollution...
parameters like e. g. COD, BOD and TSS. In these cases it proved to be advantageous to select the calibration samples manually in order to exclude this distortion.

- First order background signal changes can only be taken into account, if they are represented within the calibration data set. Background changes of a higher order will reduce the goodness of fit of the calibration model.
- Major influences on the spectra that are not covered by the respective laboratory measurements will appear like a “background” fluctuation, although it might be possible to identify and compensate for this influence.

In the specific case of the textile industry effluent one is confronted with colors. Colors show in any cases absorption in the visible spectral range and sometimes as well in the UV range but they are barely covered by the laboratory reference range, they are only covered as far as they have a significant influence on the COD values. As an example the graph below shows examples of spectra influenced by colors as well as the average spectral shape of the calibration data. The most important influence is that colors cover the entire visible range thus hampering a simple turbidity compensation.

A further difficulty in the specific case consisted in the frequent occurrence of distorted spectra due to air bubbles or other hindrances in the optical measurement path. These spectra were identified by graphical inspection and occurred due to lack of experience in installation of the prototype. The figure below shows the straightforward method for the removal spectra. Spectra
below a certain level have been considered as distorted and thus have been excluded from calibration.

![Absorption spectra graph](image)

**Figure 4: Different straight absorption spectra**

As a result of the different steps of data evaluation the table below compares the result of different approaches of data evaluation. The first column gives the coefficient of determination for a conventional linear regression at 254 nm with manual elimination of distorted spectra. The second column shows also the results for the best single wavelength (270 nm) the third column is based on automatic outlier elimination and selection of the best single wavelength and finally column four is based on automatic outlier elimination and automatic selection of several appropriate wavelengths. It can be seen that both the advanced automatic data evaluation as well as the possibility of wavelength selection yield a significant improvement of the goodness of fit.

This feasibility study was confronted with very harsh conditions like color and other matrix changes, extremely high dynamic changes of the wastewater composition and failures of the in-situ installation. It could be shown that a conventional technique like SAC 254 could not produce any results in this case, but improved data evaluation by a local calibration procedure and the availability of a multi-wavelength measurement can improve the results as compared to existing techniques.
Table 2: Coefficient of determination by different measured values

<table>
<thead>
<tr>
<th>Data set</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD calibration data</td>
<td>&lt;0,25, 0,42</td>
<td>0,55, 0,70</td>
<td></td>
</tr>
<tr>
<td>COD validation data</td>
<td>-</td>
<td>0,5, 0,55</td>
<td></td>
</tr>
<tr>
<td>Soluble COD calibration data</td>
<td>&lt;0,25, 0,35</td>
<td>0,5, 0,65</td>
<td></td>
</tr>
<tr>
<td>Soluble COD validation data</td>
<td>-, 0,42</td>
<td></td>
<td>0,55</td>
</tr>
</tbody>
</table>

However it is assumed that these preliminary results are far from the potential of the technique. Therefore two considerations about possible improvements are made:

- The calibration data do not comply optimally with the criterion of identity between the sample measured in-situ and the sample submitted to reference analysis. Small changes of the experimental procedure could result in significant improvements. Especially at this measurement site the possible errors should not be underestimated. The dynamic changes are in the order of several seconds to minutes due to the batch procedures of the textile industry and due to the dynamics of rainfall runoff. The improvement consists in an automatic grab sampling procedure that is triggered by the spectrometer itself. At the moment and for the whole duration of sampling for reference analysis also a fast acquisition of spectra is initiated.

- Another improvement concerns compensation for colors. The spectral evaluation includes curve fitting procedures for substances where the pure substance spectra are available (e.g. Benzene, Nitrate..). If the spectra of the colors would be available they could be introduced into the curve fitting procedure. Then they would be a measurement parameter instead of a disturbance.

Conclusions

The floating online probe for measurements in combined sewer systems makes it possible to record the process-dynamics of the storm-weather flow and to enumerate the discharge into the sewers. In combination with an online flow measurement device, the current pollutant load can be calculated, thus making effluent based discharge fees possible.

Not only the results derived from the obtained measurements but also the successful work carried out with the prototype in combined sewer systems encouraged the development of a new measurement equipment. This new device is currently being used in the research project. The optimization of the keel's size and shape resulted in the development of the prototype. Rope and cable duct have also been optimized. The submerged depth measured from the window is now approximately 15 cm. For measurements carried out in low dry weather flow, it is essential to provide an artificial stainless steel channel in order to enable the system to function.
Another possible application of the data is a detailed dynamic simulation of the sewer system. In combination with the well established dynamic simulation of waste water treatment plants, a real time control strategy for the combined system of waste water treatment plants and sewer systems is now possible.

References


