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REPORT

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CONTINUOUS MONITORING OF COMBINED SEWER OVERFLOWS IN THE SEWER AND THE RECEIVING RIVER: RETURN ON EXPERIENCE
Project acronym: MIA-CSO

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Title

Continous monitoring of combined sewer overflows in the sewer and the receiving river: return on experience

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Extended Abstract

This report presents practical field aspects gained during two years of monitoring with state-of-the-art spectrometers and ion-selective sensors, combining (i) continuous measurements of the quality and flow rates of combined sewer overflows (CSO) with (ii) continuous measurements of water quality parameters within the urban stretch of the River Spree. It describes the set-up and the implementation of the monitoring and evaluates the outcomes and experiences towards "lessons learnt".

The challenge of CSO monitoring is their event-based and highly dynamic nature during rain events. Applied online sensors allow dynamic measurements of CSO and water quality impacts for a wide range of parameters. However, the success of online monitoring campaigns depends highly on three main considerations.

Firstly, the representativity of the measurement station. The location of the probe must be representative of the concentration over the entire cross section of the sewer or the river. Further criteria have to be considered for the selection of the monitoring sites (e.g. easy access to the probes for maintenance) (chapter 2).

Secondly, the quality of the raw measurements. External conditions can influence the quality of measurements and lead to wrong values or outliers.

– To avoid drifts, probes need to be cleaned and checked regularly. We found that monitoring stations must be visited at least once a week for functional check-ups. During the two years of monitoring, the maintenance methodology have been continously improved to ensure the best measurement conditions (chapter 3).

– But even under state-of-the-art operation of the probes, some values can be affected by errors and lead to misinterpretation. Thus, a validation step is required to detect wrong values and separate them from valid values. Given the large amount of data, an Access-based tool has been developed to support semi-automatic validation of monitoring data (chapter 4).

Lastly, the calibration of raw measuments and the determination of uncertainties is critical. Online probes were not able to provide accurate measurements without being calibrated to local conditions with parallel laboratory measurements (online probe refers in this document to spectrometer and ISE-Probe). A Monte-Carlo method was adapted to perform regressions between raw measurement and lab values, which allows considering both uncertainties of sensor and lab chain. For instance, total uncertainty of the UV/VIS probe was between 15 and 30% for chemical oxygen demand (COD), accounting for errors from sensor, laboratory and field (representativity of site). The uncertainties in concentration and flow measurements lead to an uncertainty in CSO COD load between 20 and 70%, depending on the average concentration and flow of the event (chapter 5).

In order to gain grab samples and provide high quality calibration, an automatic sampler has been installed at the sewer monitoring. However, for operational purposes, a sewer operator will expect to gain quality online data without the effort and costs of sampling each CSO. In order to estimate the optimal sampling effort, we investigated how many events (or how many lab measurements) are necessary for calibration depending on aimed at uncertainty. From a set of 12 sampled CSO events, we simulate all possible random combinations of events and calculated each time the resulting measurement uncertainty (chapter 5.5). Results shown in Figure A indicate that at least 7 random events need to be sampled to calibrate the probe reducing uncertainties of COD measurement under 30%. It has to be noted that the concentration range of the grab samples has a high influence on the quality of the calibration. A similar analysis considering only events with high lab variations (range > 500 mg/l) showed that then only 4 events must be sampled to reduce uncertainty under 30%.
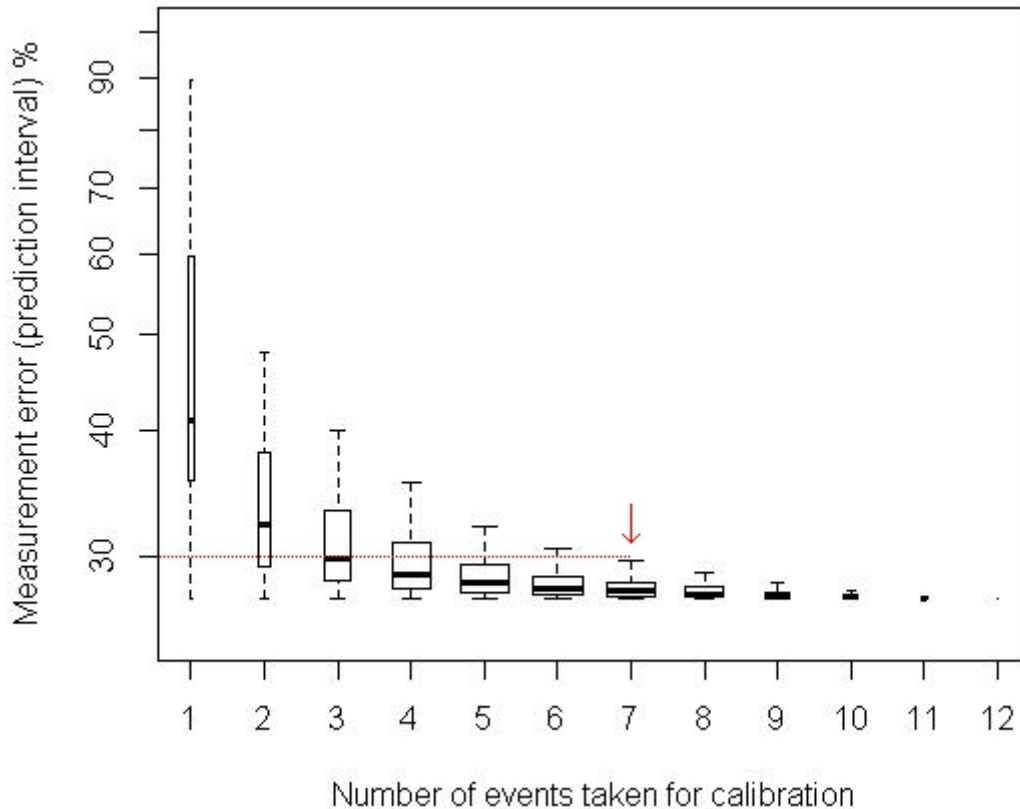
Figure A. Boxplot (mean; 5,25,75,95 percentile) of measurement error for COD according to the number of events used to build the calibration function.

Considering these results, we recommend parallel short sampling campaigns with autosamplers (grab sampling) for application of spectrometers for CSO monitoring. If the lab measurements cover the entire range of water quality variations, a minimum of 3-4 rain events should be sampled to build an accurate calibration function with acceptable uncertainty. If sampled concentration range is exceeded by later measurements, new sampling campaigns should be planned.

Since both sensor and autosampling results were available, CSO COD loads have been calculated using both spectrometer and lab values (chapter 6). Results indicate that load calculated with lab samples are within the error range of the loads calculated with spectrometer values. However, the frequency of grab sampling should be less than 10 minutes, to match concentration peaks and quick quality variations in our case. For the purpose of CSO load calculation, autosampler-based monitoring remains a cost-effective alternative to online probes. For a dynamic description of CSO (pollutant sources, mass/flow balance, etc.), autosampler-based data are limited by the minimal sample frequency and the sampling capacity. Investment and effort of online monitoring can overcome these limitations.

For river monitoring, online probes enable measuring water quality variations with an acceptable uncertainty, if the probes are properly calibrated. Here, autosamplers are clearly limited by their sampling capacity as the impacts are spread on several days in the case of the River Spree. Since no autosampler was available during the two monitoring years no clear correlation could be established for the spectrometer parameters (TSS, COD, BOD). As the manual approach often fails to catch CSO impacts, an autosampler has been purchased for the last monitoring year in 2012.

For NH_4^+ measurement, the ISE probe has been successfully calibrated performing monthly NH_4 measurements in a bucket of river water spiked with ammonium standard solution to reach values in the range expected during CSO (1-2 mg/l).

Table of Contents

Chapter 1 How to use this report ?

This document is aimed at practicioners; it describes the set-up and the implementation of the integrated monitoring and evaluates the outcomes and experiences as "lessons learnt" along the following structure:

Chapter 2   Online monitoring plannification and design:
review of Report D2.1 (Rouault, 2010)

Chapter 3   Maintenance of online probes:
general description

Chapter 4   Data management:
data storage, database tools for validation, calibration and metadata management

Chapter 5   Calibration of online probes and uncertainties:
calibration method, uncertainty calculation, probe precision, optimal sample strategy

Chapter 6   Comparison of online probes with autosampler-based monitoring:
Precision, advantages and drawbacks of both spectrometer and autosampler for the purpose of CSO loads calculation

Whereas the above chapters describe and exemplify the different monitoring aspects, details on sensor types, maintenance, etc. as well as laboratory protocols are given in the appendices:

Appendix A Factsheets instruments CSO monitoring
Details about sensors and maintenance

Appendix B Risk and safety information

Appendix C NH4 sampling protocol

Appendix D Spectrometer sampling protocol

Chapter 2
Planification and description of the integrated sewer and river monitoring

Starting point of the presented monitoring was the aim to "provide a two years continuous dataset of flow and water quality parameters at one main CSO outlet of the Berlin combined sewer system and parallel in the receiving water, River Spree. This information will be used

- to identify, analyse and describe physical and biochemical processes caused by CSO in the receiving water

- for the adaptation, calibration and validation of the river water quality model QSIM (cf. WP3.3).

This study focuses on river stretch of the Spree (Stauhaltung Charlottenburg)."[1]

Section 2 presents (i) criteria used in the planning process, (ii) description of the implemented monitoring and (iii) a brief review of the planning.

2.1 Sewer monitoring

2.1.1 Site selection

As the impact of CSO in the receiving river is of interest, the sewer monitoring was not planned in the combined sewer but in an overflow sewer collecting discharges from several CSO structures during overflow events. There are 50 CSO outlets discharge overflows from 220 CSO structures within the investigated river stretch. For the site pre-selection, data about CSO volumes and frequencies from simulations with an existing dynamic sewer model were taken into account.

Further criteria considered for the site selection were (as summarized in Bertrand-Krajewski *et al.* (2000)):

(i) no planned restructuring measures within the combined sewer system discharging into this outlet during the monitoring period,

(ii) access to essential infrastructure such as electricity, water and internet,

(iii) exposure to vandalism,

(iv) ability to obtain permission to install monitoring equipment,

(v) spatial proximity to the institution performing the study, as well as

(vi) suitability of the local shape of the overflow sewer and flow structure for flow measurements.
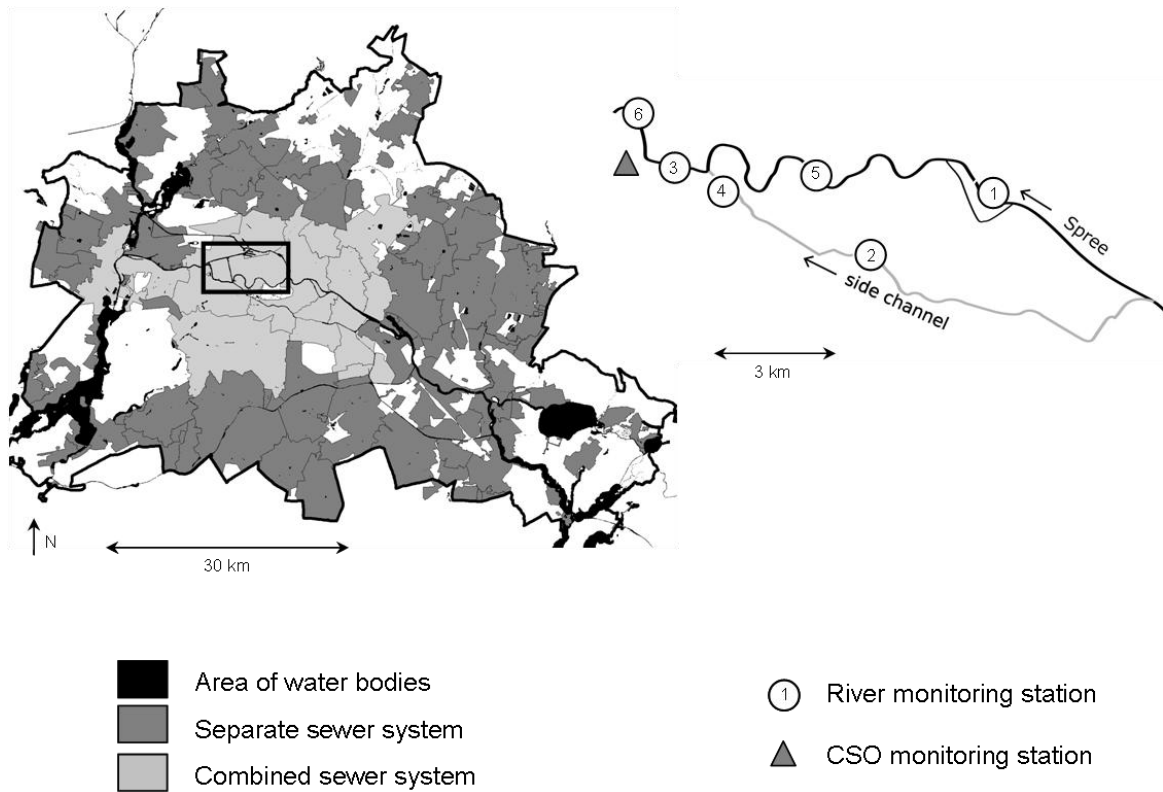
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[1] Proposal MIA-CSO, 4.3.2009

Figure 1. Situation of the integrated monitoring in Berlin. Triangle is selected CSO monitoring site. Circles 1-3 were current river monitoring sites operated by the Senate of Berlin regarding water quality parameters, circles 4-6 were planned and equipped for river monitoring.

The implemented monitoring is located in an overflow sewer in "Stallstrasse", downstream of 2 overflow structures, about 400 m upstream of the outlet to the River Spree (Figure 1). Authorization for a site on the same sewer but closer to the river was not granted by the property owner. At the monitoring site, the sewer has a cross-section of 1550 / 2100 mm (arch pipe). During dry weather, it is filled with about 1,30 m backwater from the River Spree (depends on the water level in the River Spree); during CSO, combined sewage from two CSO structures is discharged through this sewer into the River Spree. Expected CSO discharges characteristics calculated for a standard rain series (year 1997) with Infoworks CS are shown in Figure 2.
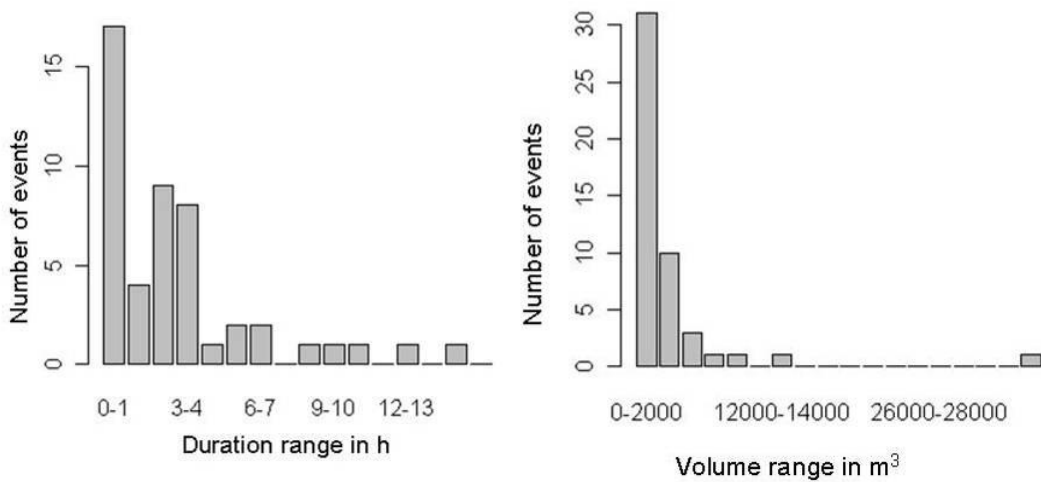

Figure 2. CSO characteristic calculated by Infoworks model for the selected CSO monitoring site Stallstraße in 1997.

Figure 3. This pictures shows the main CSO oulet discharging in the monitored overflow sewer. On the right side of the picture flows wastewater in the combined sewer system. The overflow threshold is composed of two parts: a first level of brick and 40 cm at the top of wood. The wood part was removed at the beginning of 2011 to decrease the CSO threshold.

According to the simulations, the selected CSO outlet was estimated to account for ~15% of the total annual Berlin CSO volume and load. Apart from having one of the highest discharge volumes, decisive reasons for the selection were (i) that no restructuring measure was planned within the sewer system discharging into this outlet during the monitoring period and (ii) conditions for feasibility of operation, such as access to the monitoring site or suitability for flow measurements were all favourable.

2.1.2 Design sewer monitoring

The monitoring aimed at using online sensors to provide continuous flow and water quality measurements. Given this precondition, flow was measured directly in the sewer, whereas water quality parameters were measured in a bypass (Figure 4).

The decision installing water quality sensors in a bypass and not directly in the sewer was taken considering advantages and drawbacks of both configurations described in Gruber *et al.* (2006). Main arguments were the difficulty to access the sewer regularly and the lack of Ion Selective Electrode (ISE) probes certified for ATEX (environment with an explosive atmosphere) on the market. A hybrid solution combining direct measurement and a bypass configuration was not considered for logistic simplification.
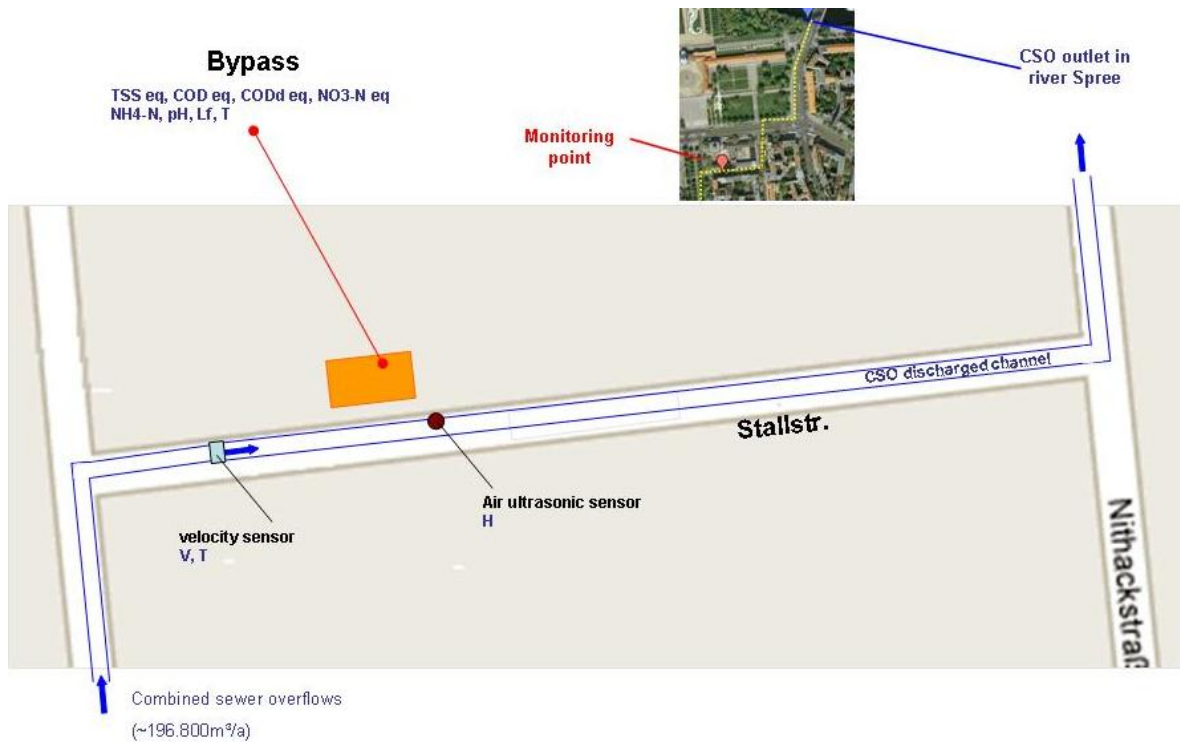
Figure 4. Overview flow and quality monitoring at CSO outlet

Flow measurement

Flow is calculated each minute by considering water level and average velocity. The velocity is measured within the medium using two sensors based on the ultrasound reflection principle, using the cross correlation method from Nivus company. Two velocity sensors are placed in the sewer about 30 m after a 90° angle (Figure 4). Two sensors were installed (Figure 5) because the installation had to be done by scuba divers (during dry weather the sewer is filled with about 1,30 m backwater from the river Spree), which is complex and costly. If one sensor is covered by mud and sediments, flow can still be measured with the other one. In addition, two sensors provide higher accuracy, particularly within a sewer of this dimension.
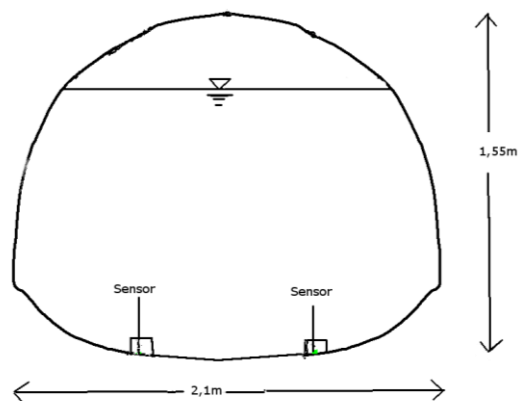

Figure 5. Profile of sewer with position of velocity sensors

Water level is measured in the sewer under a manhole using air-ultrasound principle. The temperature in the sewer is also measured by velocity sensors. Data from the sensors are collected by a data logger (OCMProCF, Nivus company) set up in a container situated directly above the overflow sewer on the pavement (Figure 6-7).

Water quality measurement

Water quality parameters are measured in a bypass installed in a container (Figure 6-7). Using a peristaltic pump, water is pumped from the top third of the water depth in the sewer to a flume, in which the following sensors are immersed.

- UV/VIS spectrometer (spectro::lyser, s::can company) for the measurement of absorption water spectra which enable calculating equivalents of chemical oxygen demand (CODeq), dissolved CODdeq, total suspended solids (TSSeq), total organic carbon (TOCeq) and biological oxygen demand (BODeq),

- Ion selective probe (ISE, ammo::lyser, s::can company) for ammonium (NH_4), potassium (K) and pH measurements,

- condu::lyser from s::can company for electrical conductivity (EC) and temperature (T) measurements.

Both ammo::lyser and condu::lyser are cleaned automatically with pressure air every 20 minutes for the spectro::lyser and 1 hour for the ammo::lyser.

Figure 6. Bypass, autosampler, pump and probes for measurement of water quality in the container
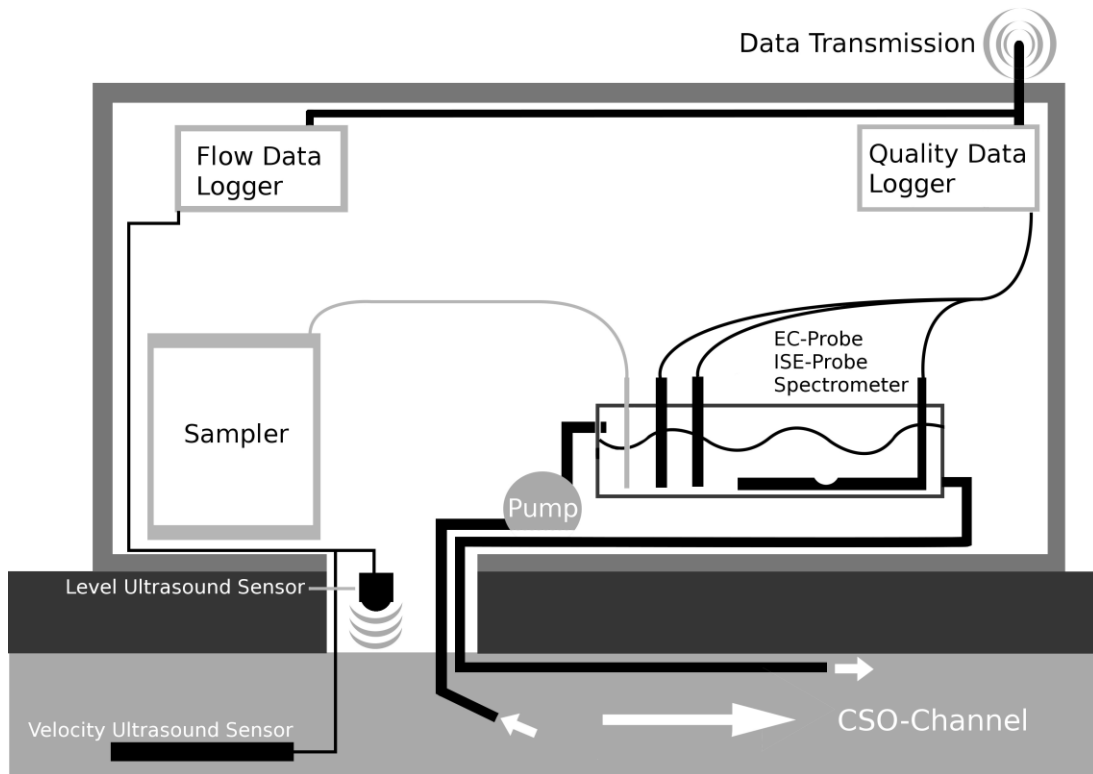
Figure 7. Overview bypass for measurement of water quality parameters

Water quality probes are connected to the data logger cons::tat, which allows data displaying, transfer, as well as probes set up and calibration. To avoid flooding from the bypass in the case of a system malfunction, a pressure sensor controls the water level in the flume and stops the pump if necessary. An other warning sensor stops the pump in case of damage of the pump flexible tube. A plastic grid has been installed close to the inflow pipe in the flume to block undesirable pumped objects and avoid the disturbance of measurement.

Complete description of sensors and devices (pump, probes, etc.) with brand names is given in appendix A.

For validation and calibration of online probes, laboratory instruments were purchased (Figure 8) and installed in the container. Grab samples can be analysed with test cuves from Hach Lange on site without time delay for transport to the lab and so probe transformation can be avoided.

Figure 8. Laboratory instruments for sample analysis on site: pipette, thermostat and photometer.

Data transmission

Both data logger OCMpro and cons::tat are connected to an industry computer, which send continually data to KWB through UMTS. Important operating information are also sent to KWB, such as the status of the pump (on/off), failure messages from data logger, damage of the pump flexible tube, abnormal level in the flume. This computer is equipped with the scada system "Nicos" that allows for operation control, data display and data evaluation.

2.1.3 Planning versus reality

The careful selection and planning phase of the monitoring allowed a smooth implementation of monitoring activities. Nevertheless some adaptations were necessary, which are outlined briefly below.

During the first monitoring year it was noticed that the discharged volume and event number were much lower than expected (in 2010, CSO volume was about 10000 m^3 in 4 events, annual expected volume according to sewer simulations was 200,000 m^3 in 29 events). Detailed evaluations revealed that the CSO weir height of the main CSO structure discharging in the monitored overflow sewer, which was used for the simulations was wrong, due to errors in the outlet plan. A new measurement campaign showed that the threshold was actually 56 cm higher than described in the last plan available. In reaction the 40 cm wood crest of the weir could be removed at the beginning of the second monitoring year (2011), in order to increase the number of observable events in the monitored sewer (Figure 3). In parallel, the crest height of another CSO outlet situated upstream in the combined sewer system and discharging into a different overflow sewer was increased in order to ensure the same global number and volume of CSO in the catchment (simulation results from Berliner Wasserbetriebe, 2010). As a result of the measures, observed CSO volume and event numbers were increased successfully in 2011 (11 events with a total volume of 33470 m^3) but remained below the originally anticipated values.

Regarding the monitoring itself, samples for calibration were taken manually during CSO, when we managed to be present during the event in 2010. Since it is impossible to be present at the monitoring station immediately when CSO occur and calibration effort turned out to be higher than anticipated (see section 5), a transportable refrigerated automatic sampler (by Hydreka company) was installed at the beginning of the second monitoring year 2011 (Figure 6). In order to ensure the homogeneity and representativity of the samples, the water intake as been fixed in the flume on the spectrometer structure.

2.2 River monitoring

2.2.1 Site selection

Independently of the project, the Berlin Senate Department of Health, Environment and Consumer Protection (SenGesUmV) conducts a continuous flow and water quality monitoring of the River Spree. Flow measurements are performed in the River Spree and in its side channels. Moreover, continuous measurements of standard water quality parameters (DO, pH, temperature and specific conductivity) are carried out at several monitoring stations (monitoring stations 1 to 3 in Figure 1). Monthly grab samples are taken at several spots along the River Spree and analyzed for a number of chemical and biological parameters.

In a first step, an assessment was made whether the current river monitoring (station 1-3, Figure 1) delivers sufficient information for this study; i.e. if CSO impacts can be detected and if the numerical models can be calibrated. 8 years of river monitoring data were analyzed and related to rain and CSO occurrence in order to assess temporal and spatial effects in the river during and after CSO events (Riechel, 2009). Assessment of existing continuous DO monitoring data revealed that DO concentration is very sensitive to CSO influence. After important rainfall events with CSO, DO concentration typically declines (Figure 9). Though continuous information about NH_4 were not available, a simplified assessment based on measured pH values indicated that NH_3 toxicity is less severe than DO depletion.

Interesting current monitoring stations for this study were identified to be Station 1, localized at the beginning of the river stretch, and Station 3 within the river stretch after its confluence with the side channel Landwehrkanal (Figure 1). Station 2 in the Landwehrkanal is of interest; however its position is upstream of a great number of CSO outlets. As a result, it is not representative for the quality of water that flows into the River Spree further downstream. The need for an extension of the current monitoring was pointed out, since the following information was missing.

- Boundary condition in the side channel Landwehrkanal before its confluence with River Spree. This channel often shows high DO insufficiency, particularly in summer and after CSO discharges.

- Situation at the end of the studied river stretch. This station is of high importance for model calibration, but also for the assessment of the impact from the monitored CSO outlet.

- Situation within the river stretch.

- Extension of measured parameters to evaluate loads of organic matter and NH_4 during CSO at the start and the end of the studied river stretch.
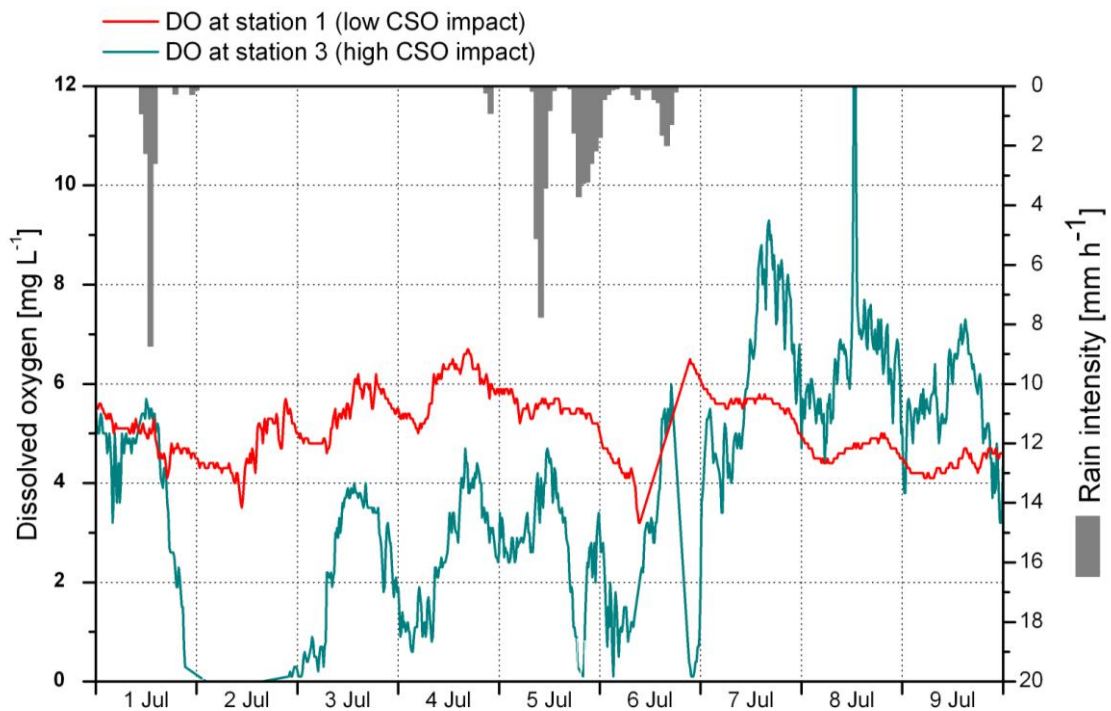

Figure 9. Continuous evolution of DO concentration after a typical rain event in July 2005. Data obtained from continuous measurement by the city of Berlin at the stations 1 and 3 (See Figure 1).

Potential monitoring sites were preselected based on the above requirements. In a second step, final selection was done by examining the following points:

- The river topology and the position of CSO outlets.

- Local conditions during on-site inspections. The river bank has to be accessible and the site should not be prone to vandalism. Representative sites are required to be set along or close to the river banks, monitoring stations must remain accessible for weekly maintenance purposes.

- River section homogeneity. As measurements have to be done at one specific location in the river section, water have to be relatively well mixed over the whole cross-section.

The last point was a major concern, since homogeneity cannot be expected in slowly flowing, wide lowland rivers. To evaluate river homogeneity, DO distribution was measured along and across the River Spree using a portable optical DO sensor (ProODO, YSI). Firstly, the basic state of the river was monitored, i.e. a normal situation during dry weather conditions without influence of CSO. Thus, the representativity of water quality measurements at a preselected site for the specific river stretch can be checked. Since it is important to compare measurements at the banks (where a potential monitoring station could be situated) with the middle of the river, DO was mostly measured at bridges close to pre-selected sites for practical reasons. For sites shown to be representative under dry weather conditions, further DO measurements were also conducted after CSO discharges. Given the study's aim, selected monitoring sites must be representative for the specific river stretch in both cases.

An example is given for the river stretch at existing monitoring station 3, after the confluence of the Landwehrkanal and the River Spree (Figure 10). The purpose of the measurements was to confirm the relevance of this already existing station; i.e. to check whether water bodies of the two tributaries are completely mixed.
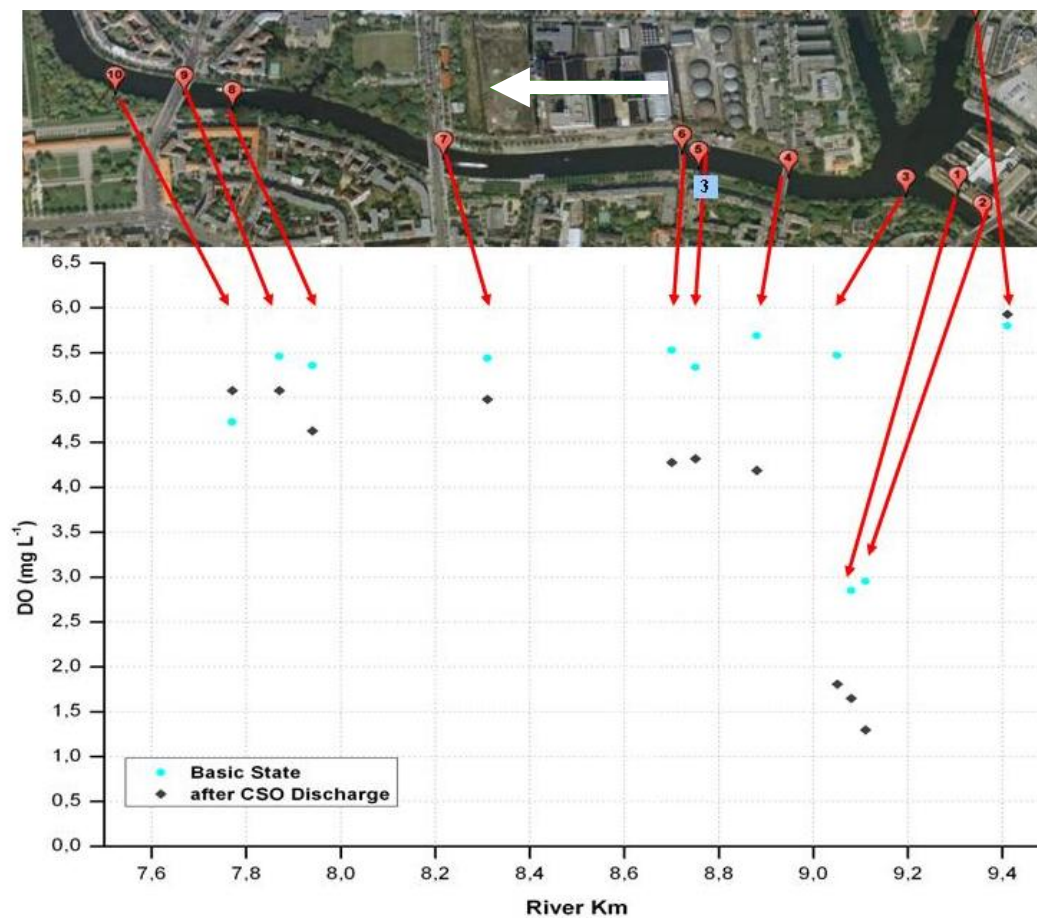

Figure 10. Evolutions of the DO concentration along the preselected river stretch during dry weather (blue) and after CSO discharges (grey) to check the site pertinence. White arrow indicates flow direction of River Spree.

In terms of DO levels, mixing across the river at station 3 turned out to be homogeneous even after CSO discharge (Figure 10). This is surprising regarding the short distance to the point of confluence. One could argue, that a measurement station further downstream (e.g. at river km 8.3) would be more relevant, since there is no real DO evolution downstream from this site. Nevertheless, the slight deviation does not justify the effort required to displace the current station.

Finally, pre-selected stations 4-6 were validated positively by applying the same methodology and therefore selected as new monitoring sites for the program (Figures 1, 11,12 and 13).

Figure 11. Location of planned river monitoring station 4 in channel "Landwehrkanal"

Figure 12. Location of planned river monitoring station 5 within river stretch "Stadtspree"

Figure 13. Location of planned river monitoring station 6 at the end of river stretch "Stadtspree"

2.2.2 Design river monitoring

Following the detected information gaps, the three existing monitoring stations (1-3) and the three new monitoring stations implemented for the project (4-6) are equipped to measure standard water quality parameters (pH, DO, T, EC) with classical probes (e.g. WTW TechnoLine). In addition, NH_4 concentration is measured at the end of the river stretch (station 6) with ISE (ammo::lyser, s::can company) and TSSeq, CODeq, CODdeq, TOCeq and BODeq are monitored at the beginning and the end of the stretch (stations 1 and 6), using UV/VIS spectrometer from s::can company. These additional parameters will only be measured at the beginning and at the end of the river stretch since cost and maintenance efforts are high.

Figure 14. Location of planned river monitoring station 6 at the end of the river stretch

Figure 15. Instruments of monitoring station 6. Ammo::lyser above his pipe structure on the bottom left photo. Spectro::lyser and his metal structure on the right photo, zoom on the probe on the top left photo.

At station 6, probes are fixed with metal supports and immersed directly in the river while data logger and compressor for automatic cleaning are closed in a locked box on the bank (Figures 14-15). The main advantages of this structure are the low price and the construction flexibility (the whole station can be easily removed). However, the probes have to be removed in winter because of temperature and potential damages due to ice.

In contrast station 1 is situated in a small house close to the river bank. The spectrometer could be operated in a bypass of an already existing monitoring station from the Senate Department of Health, Environment and Consumer Protection. A flow derivation has been constructed with a bypass fitting for the spectrometer. A compressor cleans automatically the measurement windows every 20 minutes. A data logger con::stat has been installed to display and save the data (top right corner, Figure 16).

Figure 16. Location and probe's installation at the upstream river monitoring station 1

2.2.3 Planning versus reality

In order to calibrate the probes, samples are taken manually during CSO events and on a regular basis in order to get seasonal variations of the parameter. As for sewer monitoring, since it is impossible to be present at the monitoring station immediately when CSO occur and calibration effort turned out to be higher than anticipated (see section 5), a transportable refrigerated automatic sampler (by Hydreka company) was purchased at the beginning of the third monitoring year 2012 and installed at station 6.

Chapter 3 Monitoring maintenance

The following paragraphs present the general maintenance organisation and point out some major difficulties. A detailed description of sensors and main devices of the integrated monitoring, as well as suggested maintenance is presented for each device in Appendix A. A risk and safety plan for operators is available in Appendix B.

3.1 Security

The operation of monitoring stations deals with risks mainly due to exposure to sewage and chemicals. A risk and safety plan has been established (see appendix B), in which risks, prevention and actions in the case of accidents or contact with sewage/chemicals are specified. This plan must be signed annually by all staff members working in the container; with it they confirm they are informed about risks and will consider all suggestions for prevention. Furthermore, a first-aid training is recommended.

3.2 Maintenance

The sewer and river monitoring stations need to be visited once a week for periodic cleaning and maintenance of the instruments in order to ensure continous operation of all devices. The main tasks are the cleaning and the referencing of the probes, the data transfer and the time synchronisation of all devices.

Detailed information about devices, maintenance tasks and optimal frequency are listed in Appendix A. The recommended frequency of tasks are derived from operation manuals by the manufacturer and from our experience in the special case of river and sewer monitoring.

The stations are always visited on Wednesdays, in the middle of the week, in order to get the possibility to return on site during the week in case of any issues and to ensure that the stations are working fine before the week end. It is recommended that maintenance of the stations is performed by two persons for safety reasons (wastewater, station close to river bank) and to reduce the duration on field. However, most operations can also be performed by one single operator. The visit to each station lasts between 1 and 2 hours; thus the complete maintenance of the integrated sewer and river monitoring is easily realised in one working day. As a consequence, a precise maintenance timetable can be set up. Nevertheless, the responsible operator should be available the entire week to be able to go on site in the case of rain events or emergency situations (for example: flood in bypass) to make sure that stations remain functional. The classical probes (pH, DO, T, EC) of the river monitoring stations operated by the Berlin Senate Department of Health, Environment and Consumer Protection are also visited once a week for maintenance.

Data quality critically depends on the sampling strategy for validation and calibration of the online sensors (see also section 5). However, even an optimal sampling campaign can lead to very low precision of the calibrated measurements, if the raw measurements from the probe are affected due to improper handling or maintenance. During the two years of operation, we continually improved maintenance methods (e.g., the use of cleaning agents) to operate the probes ensuring the best quality of raw measurements (see Appendix A for optimized approach).

Recurring problems were met in particular with the ISE Probe (ammo::lyser). The probe often registered drifts or sudden steps in time series (Figure 17), which can be caused by:

(i) Change in the medium

(ii) Concentration of interfering ions: potassium (K) concentrations can influence the voltage measurement of NH_4

(iii) Fouling of membrane

(iv) Ageing of membrane: membrane lifetime is about 6 months for river monitoring (low NH4 concentrations) and 1 year for sewer monitoring (high NH4 concentrations).
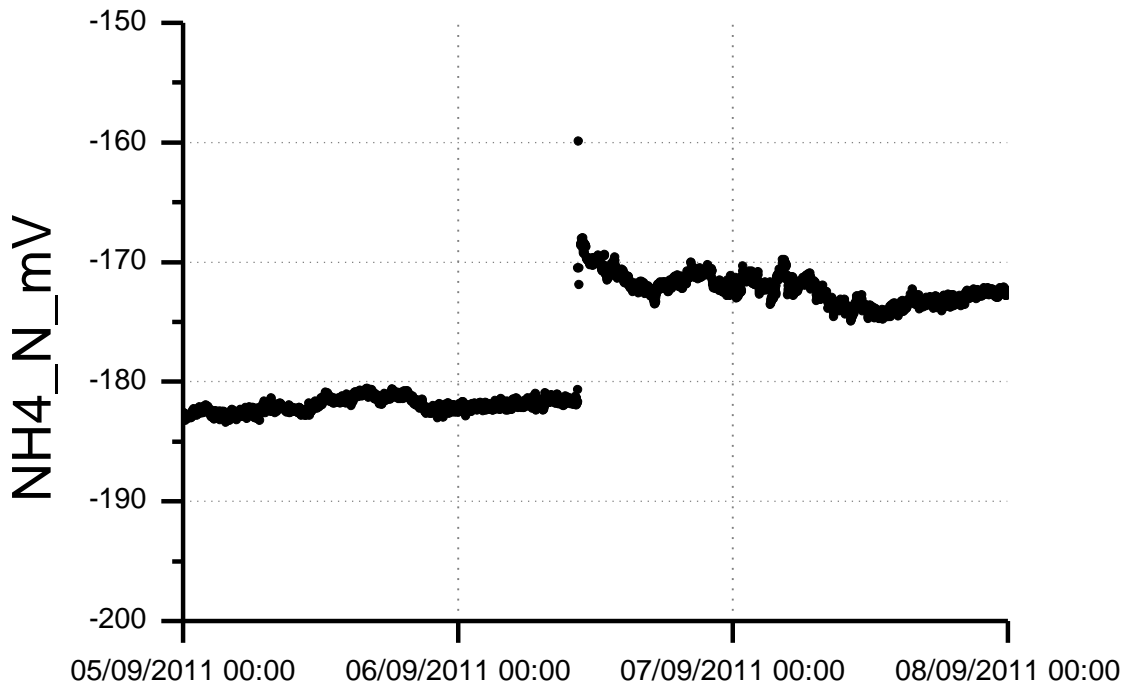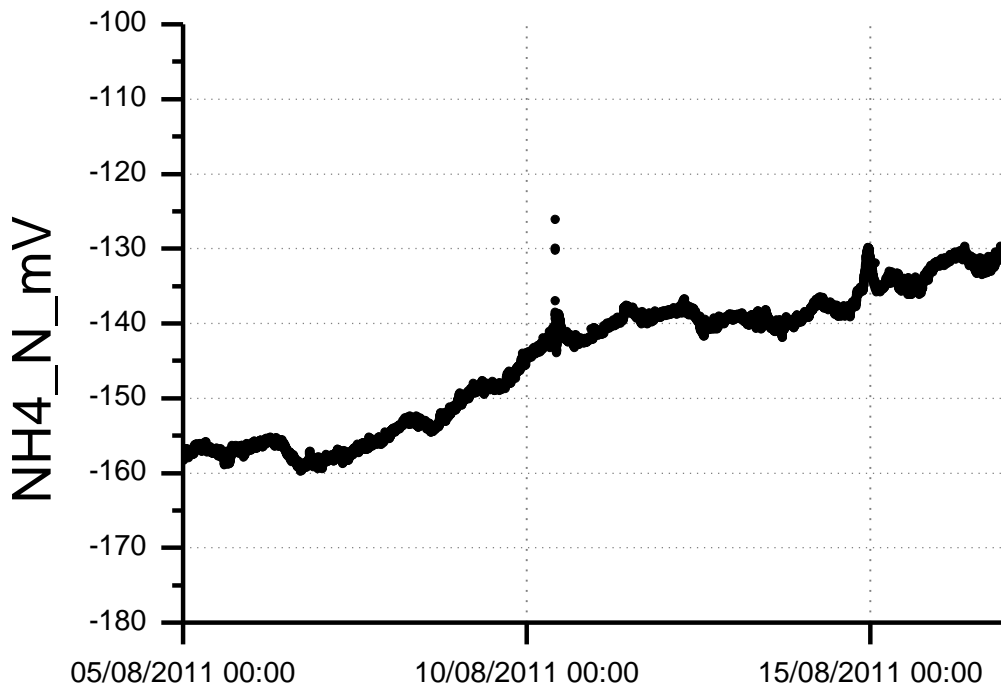
Figure 17. Examples of measurement errors at the downstream river monitoring. The graph above shows a drift caused by ageing of the membrane. The bottom graph shows a step in NH4 time series caused by the cleaning of the membranes.

To check quality of the signal (i) and level of interfering ions (ii), NH_4 and K lab measurement need to be performed every week. In our case NH_4 concentrations in the river was quite constant and varied only during CSO impacts. Lab measurement showed very low potassium variation in both river and sewer monitoring. To avoid fouling of the membrane (iii), intensive cleaning (as described in appendix A) was performed but experience showed that drifts and steps can occur even at precautionary operation of the probes. In general drifts increase with the aging of the membranes (iv). Figure 17 shows an example of measurement drifts caused by an aged membrane after 6 months of continuous operation. As membranes are costly, it is not suggested to do a preventive replacement of membranes. However, spare membranes should be available in the case that probe performance becomes poor.

In retrospect, major monitoring effort for the ammo::lyser comes from quality control and cleaning. It is highly recommended to clean the device and perform laboratory measurement each week, and to change the membrane at least every 6 months. Even under precautionary operation of the probe, good data quality is not guaranteed especially for river monitoring, where NH_4 range is very small (between 0 and 2 mg/l), in the same order of magnitude as variation due to fouling or membrane ageing.

Difficulties have also been met with the bypass fitting installation of station 1 (Mühlendammschleuse, Figure 16). After one month of operation, we noticed an increasing amount of outliers and a strong drift in spectrometer measurements (Figure 18). Problems were due to the accumulation of sediments and fouling in the inflow pipe of the probe which were resuspended each time the probe was cleaned automatically with compressed air. The problem could be resolved by dismounting and cleaning the pipes each week in summer and less frequently the rest of the year. In winter the pipe stayed quite clear because of the lower concentration of suspended solids. The example shows the advantage of an open flume used in the sewer monitoring compared to a bypass fitting, where probes are not visible (a system often suggested by manufacturers).
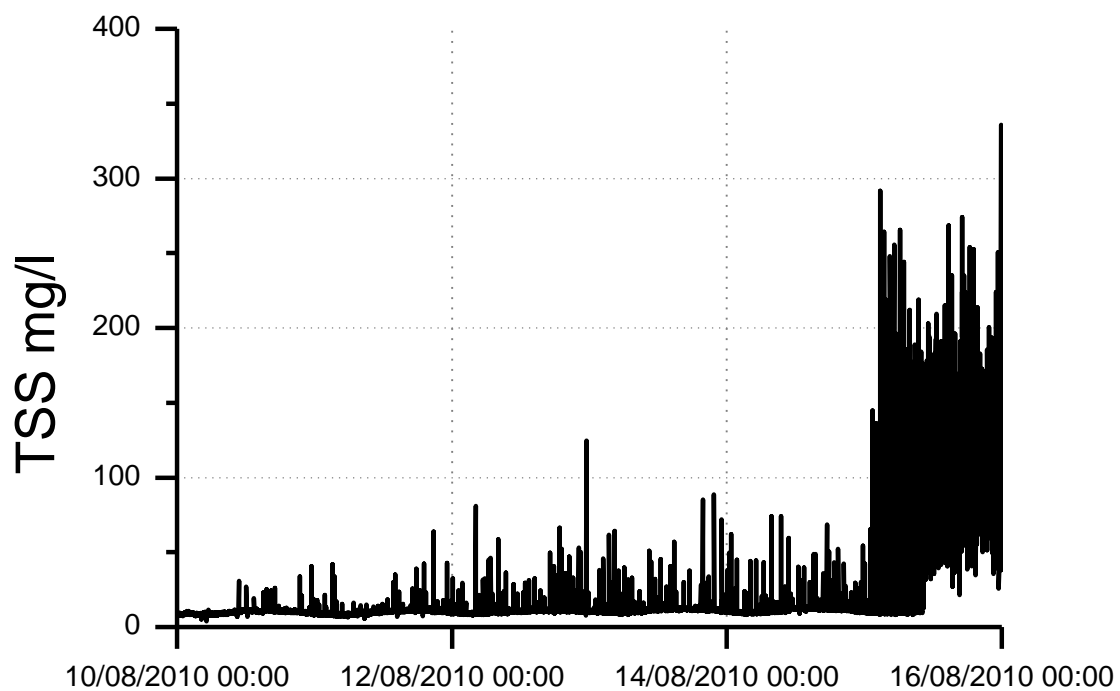

Figure 18. Drift measurements at the river monitoring station1

3.3 Warning and event supervision

For the sewer monitoring, measurement and functioning of the probes are checked every morning via the data transfer system "Nicos". If measurements are missing, the instruments need to be checked on site to see if a problem occurred. Moreover, several digital warning signals were available via "Nicos":

- Damage of the pump flexible tube: a water-sensitive sensor is activated if the tube is leaking
- Abnormal level in the flume: a sensor switches off the pump if the level in the flume exceeds a security threshold
- Failure message from flow data logger
- Functionning of the pump: a signal is sent if the pump is off (which can happen as a result of voltage fluctuations in the power supply)

The daily control of these warning signals is essential to avoid flood disages and dysfunctions. Extra intervention is planned after the observation of the warnings.

Chapter 4 Data management

A data management concept has been developed for the project in order to

- Ensure safe storage of the raw data
- Ensure data quality, i.e. the automatic detection of wrong values
- Correct raw measurements to "real" lab values (calibration step)
- Ease the further use of data (graphic, model, calculation, etc.)

In order to gather all data under the same format, files are imported automatically into an Access database. Raw data import is supported by a self-developed import tool able to handle different file formats. To ensure data quality, raw data have to be validated; valid results are separated from invalid and stored in a new database. The last step is the calibration of the measurements, i.e. the establishment of a relation between measured values and laboratory values. The next paragraphs specifies each step of the data management (schematic overview in Figure 19).
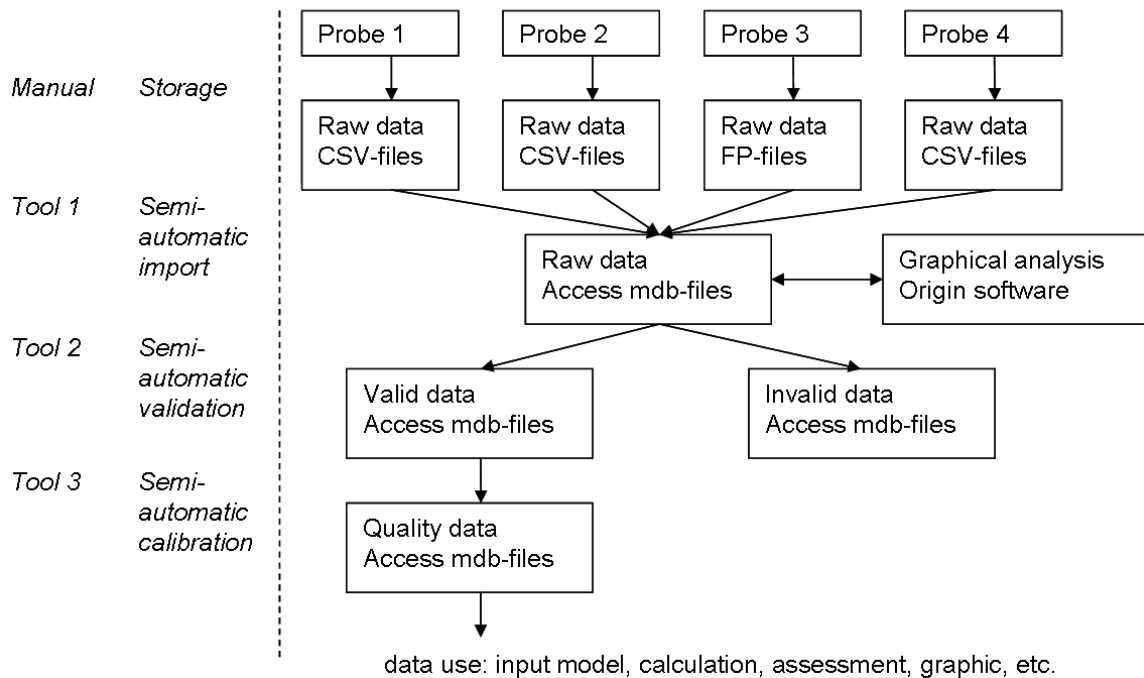
Figure 19. MIA-CSO data management steps

4.1 Data storage

Measurement data have to be stored in an easy and secure way. Each week data are saved in their original form (text files) on a field laptop; data also remain on the instrument (oldest data are automatically deleted when storage capacity is exceeded). We decided to save data directly from the devices instead of using the data sent to KWB through UTMS because spectrums measured by spectrometer are very large. Moreover, switching between analogous and digital data can lead to rounding errors. Data are then copied from the field laptop on a server (with automatic data backup) at the office each month. A password is necessary to include new data in order to avoid mistakes or data loss.

4.2 Organisation of raw data in standardized database

Raw data are saved from the devices in many files under several formats. A flexible MS Access tool (Tool 1 in Figure 20; Figure 21) has been developed to gather the data under the same format and ease the further validation of data. The tool cuts header lines, identifies parameter values according to their names and copies raw data from each selected file into a new database. Laboratory measurements performed on site or later at the laboratory are also filled in an Access database which contains the sample date and time. Given the standardized format raw data and lab measurement can be easily imported into the graphic software Origin for a first analysis.
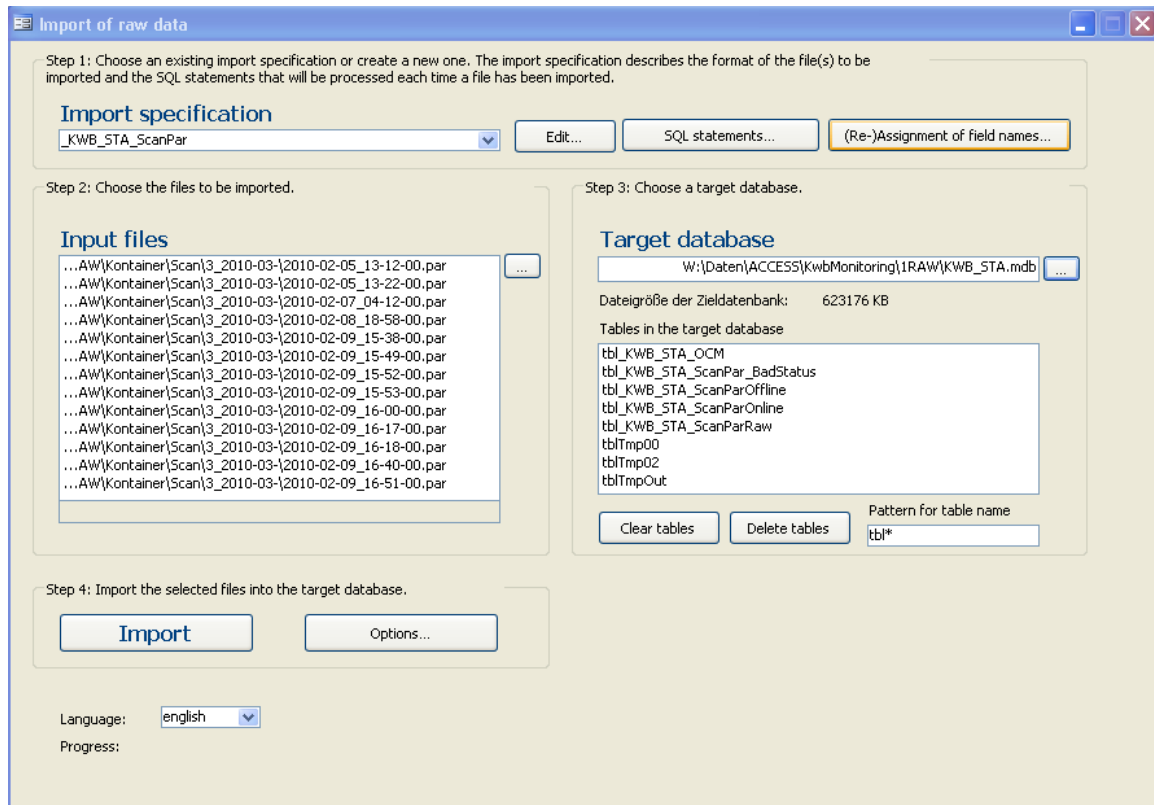

Figure 20. Screen shot of the Access-based import tool 1. The user selects files containing raw data on the left window and the output database on the right window.

Figure 21. Screen shot of the "raw data" database. Data from each station are gathered under the same format.

4.3 Validation database

Even under state-of-the-art operation of the probes, some values can be affected by errors and lie outside of their range of prediction. A validation step should detect outliers and separate them from valid values.

Data validation consists in declaring if values are valid or invalid. An Access-based tool (Tool 2 in Figure 22) has been developed in the frame of the project to support semi-automatic validation of large sets of raw data (Figure 23). Based on recommendations in Mourad and Bertrand-Krajewski (2002) three criterions and three validation marks (A: valid data, B: doubtful data, C: invalid data) are applied to the imported data in the following order:

- status of the probe,

- realistic range of the measurement,

- signal time derivative.

Each measurement receives a global mark after the application of each criterion: A if all criteria are marked A; B if at least one is B; and C if at least one is C (Figure 23). Data with global mark A are automatically extracted and secured in a new database. Data with global marks B are automatically extracted for a manual validation: they should be checked and defined manually as valid or invalid. An optimized selection of boundary values for each criterion should identify automatically valid from invalid data to a great extent and declare only few doubtful data. Doubtful data that are manually identified to be valid, are selected within "Origin" graphic software, and added to already valid data by the aid of the validation tool. Data with a global mark of C are discarded and stored in a separate database. The history of performed validation steps is also saved. At the end of the validation procedure, reliable measurement data have been extracted into a new database for further data uses.
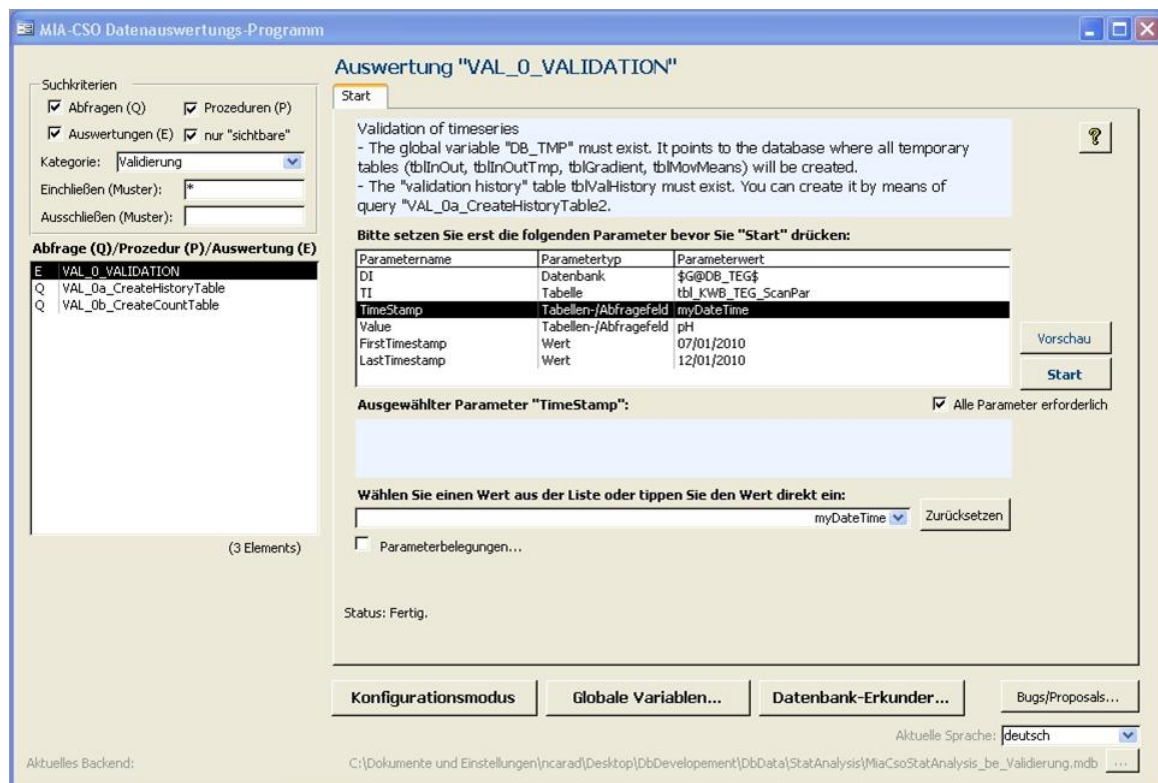

Figure 22. Screen shot of the Access-based validation tool 2. The user selects the parameter to validate, the time interval and the boundary values for each criterion (Range B, Range C, Gradient B and Gradient C). The tool generates automatically valid, doubtful and invalid data from raw data

Figure 23. Application of the validation criterion with the Access tool. Blue „A" values are valid values. Green „B" values are doubtful and should be manually validated. Red „C" values are wrong and should be discarded from the validation process.

4.4 Calibration database

This step corresponds to the calibration of validated data at each time step. Calibration curves are based on regression functions derived from data pairs of laboratory values and validated probe measurements. Coefficients of calibration equations (slope and offset for linear regression, see chapter 5) for each parameter and each station are filled in a calibration tool (Tool 3 in Figure 24).

Figure 24. Screenshot of the calibration tool. The user selects the parameter (CSB=COD) in the upper left corner, the monitoring station (STA for Stallstr., sewer monitoring station) and implements the slope and offset coefficients for several partial calibrations, with comments. In that example, a calibration function is used for 2010 (black underlined). A second function is applied for 2011 except for one event on 29.07.2011 with low concentrations outside of the calibration range.

This tool allows an easy modification of calibration coefficients. For each parameter, several calibration functions can be stored for different time intervals of data. For river monitoring,

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seasonal calibration can be found and applied for specific months of the year. For NH_4 measurements, calibration can change each time new lab measurements are performed in order to get a best fit. Comments can be added to document the origin of the calibration (samples used, outliers).

A third database named "CAL" consists of queries, one query for each parameter of each monitoring station. By running the query, the corresponding data from the validation database "VAL" are corrected by applying the linear functions saved in the calibration tool for each partial calibration period. The result of the query is a table containing calibrated data used for data analysis, load calculations and evaluations.

4.5 Metadata management

An Access based tool has been developed to save and organise metadata, i.e. all informations about instrument maintenance, operation and repair. A set of input forms guides the operator working in the container. On the main form (Figure 25) the user first selects a monitoring station and an equipment ("Device") from the combo list in the upper left corner of the form. By doing so, all actions that are defined for the selected equipment are listed under "assigned actions". By clicking on one of the entries in the list box "Filter action types" on the left, the list of actions may be filtered so that only those actions are shown that belong to a specific category, such as operation ("Betrieb"), cleaning ("Reinigung"), maintenance ("Wartung") or others ("Sonstige").

Once an action is selected, e.g. the action "Membranersatz" (replacement of membrane) in Figure 25, information about that action is given in the area "Action info" in the upper right part of the form: (i) recurrence period, i.e. how often this action needs to be done, (ii) the last time this action has been accomplished, (iii) the next time the action needs to be accomplished again and (iv) comments giving additional information about the action.

By using the lower part of the form the accomplishment of an action can be registered. The information about who performed the action and when needs to be given.

In the lower right part of the form, all actions that have to be accomplished on this day are listed under "to be performed on" (actions to do today). By clicking on an entry of that list, information about the corresponding action is loaded and the accomplishment of that action can directly be registered as described above. As soon as the action has been done and registered, the corresponding entry disappears from the "actions to do today" list and instead appears in the lower list "performed today". As soon as the "actions to do today" list is empty there are no more actions that have to be done the same day. Taking into account the information of when actions have been perfomed, the database tool automatically calculates at which dates actions have to be repeated.

The database application saves the history of actions that have been performed in the container. A specific form gives the possibility to search this history by specific actions, dates of accomplishment, user names or comments that may have been additionally stored. This options are particulary useful for the manual validation step, since outliers can be double-checked considering maintenance and operation information.

Figure 25. Form of database application for storing metadata

A specific calendar form (Figure 26) gives an overview of all the actions that were accomplished in the past and that need to be done in the future. It can be consulted before doing any maintenance. By double-clicking on an entry representing an action that has already been performed, the history of all accomplishments of the same action is shown in a separate form. Double-clicking on an entry that represents an undone action opens the main form, preselects the corresponding action and waits for registering the accomplishment of that action.

Figure 26. Calendar form in database application for metadata

Chapter 5 Calibration

UV/VIS spectrometer and ISE-Probes are in-situ probes. In the case of spectrometer, concentrations are calculated with multivariate regression techniques from absorbance measurements. In the case of ISE-Probe, NH_4-N concentrations are calculated with the Nernst Equation from voltage measurement between a reference and a measurement electrode.

A global calibration for typical municipal wastewater and river is provided as default configuration of the UV/VIS spectrometer. For the ISE-Probe, the standard Nernst equation is applied. However, due to the different composition of waste and river water a second calibration step (local calibration) is required to enhance the measurement quality. Online probes are not able to provide accurate measurements of water quality without beeing locally calibrated with laboratory measurement. Manufacturer global calibration can lead to systematic error up to 50% for COD measurements (Gamerith *et al.*, 2011).

The efforts of the monitoring operator should focus on this calibration step, as the precision of the measurement depends mostly on the quality of the regression. For this purpose, laboratory measurements are correlated with in-situ measurements. For COD measurement, with simple linear regression between lab values and concentrations obtained from the global calibration, sensor uncertainty can be reduced to an order of magnitude of 15-30%.

The whole calibration procedure can only be successful, if the following general rules for the reference samples are taken into account:

- Minimisation of errors induced by sampling : the identity between sampled liquid and liquid measured in-situ has to be guaranteed. Errors from the lab chain should be minimised (sample storage, transport and analysis).

- The entire measurement range has to be covered by the reference samples and they have to be equally distributed over this range.

In order to monitor CSO, samples should be taken during rain events to have laboratory measurements under the condition of interest. In the river, samples should also be taken on a regular basis in order to get a large range of concentrations and cover possible seasonal variations of the parameters (e.g., influence of algae on BOD concentration). Due to the short duration of rain events, it is difficult to gain manual samples of impacts or CSO events. We thus recommend to use autosamplers temporarily to ensure sufficient samples during CSO events for calibration. In the following subsections we make recommendations about the optimal number of CSO events to sample in order to reach an acceptable precision with the calibrated devices.

5.1 Sampling and laboratory analysis

5.1.1 Sewer monitoring

At the beginning of 2011, an autosampler has been purchased to gain samples during all CSO events. The maximum number of events have been sampled since to identify optimal number of sampled events for calibration for online probes users.

The autosampler starts if the flow exceed a threshold of 0.3 m^3/s longer than 1 minute. The device pumps 2 bottles of 1L each 5 minutes. As it contains 24 bottles, CSO can be sampled over a duration of one hour. When the flow begins, the water remaining in the CSO overflow sewer between the CSO outlets and the monitoring station is flushed before that the CSO water arrived at the station. Generally, the first sample is a low impacted water and the second probe (5 minutes after) has already CSO quality. A 5 minutes time-step seems adequate in order to get measurements of the entire pollutant variation and peaks (see also discussion in section 6). The sampled water and water scanned in-situ by the probe should be as similar as possible. For that reason, the intake of the sampler was fixed on the spectrometer structure close to the measurement windows. Sample duration is about 1.5 min

(purge, rinsing and intake of 2 samples of 1L). We assume that samples correspond to instantaneous spectrometer measurements made at the same minute, which may be a source of error, since CSO water quality can vary during the sampling time.

5.1.2 River monitoring

Sampling on a regular basis

As water quality varies during the year, samples are taken on a regular basis: each week for NH4, COD and CODf measurement; each month for TSS, BOD, TOC, P, PO_4, NO_3 and NO_2. The Berlin Senate for Environment already take samples each month and follows analysis for a wide range of parameters. Our monthly sampling has been shifted by 15 days to get finally measurements every 15 days for the parameters of interest. Samples are taken manually with 2L bottles very close from the measurement windows of the spectrometer at the same time of the measurement.

Samples taken on a regular basis in 2010 and 2011 indicate small variation range for the parameter of interest. Figure 27 shows COD lab measurement at station 6 (Tegeler Weg) in 2011, ranking between about 15 and 30 mg/l.
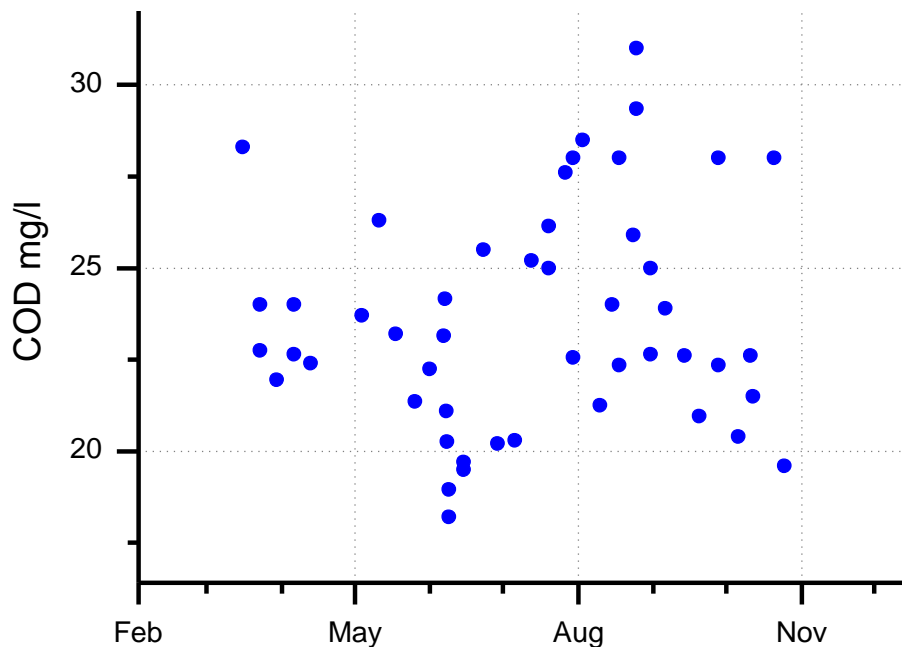

Figure 27. COD lab measurements at station 6 in 2011.

No clear local calibration could be established on the basis of the regular measurement. The variation range is too low and no reliable correlation can be set up. Figure 28 shows a cloud of points by plotting lab measurement against spectrometer measurement.
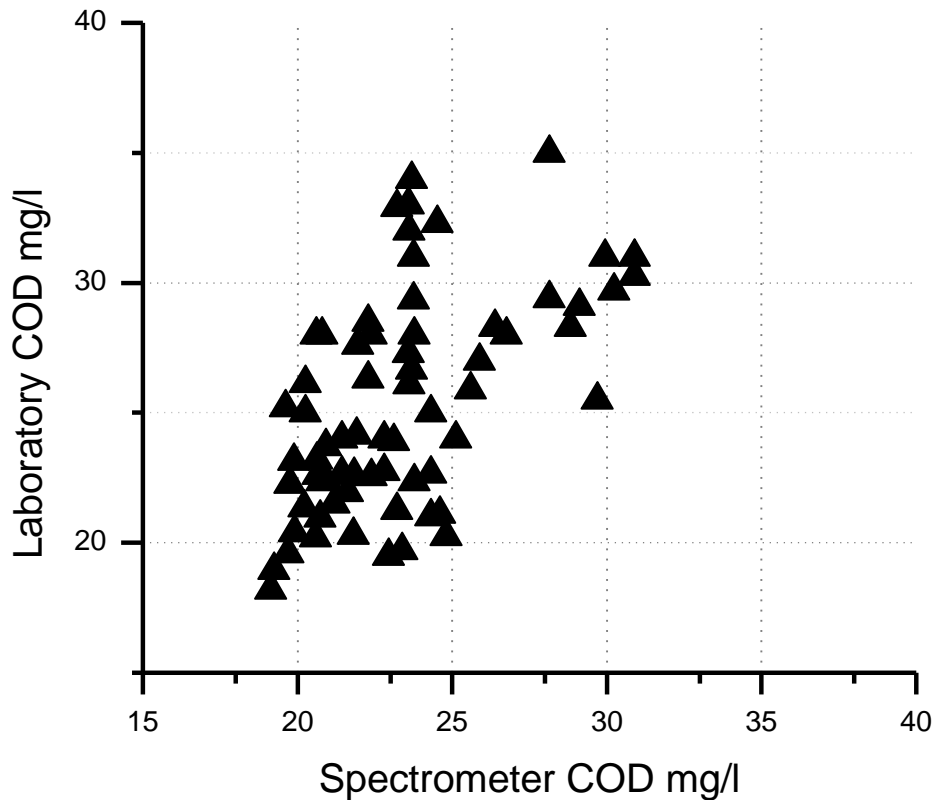
Figure 28. COD lab measurements at station 6 in 2010 and 2011 against spectrometer measurements (only samples taken on a regular basis).

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Sampling during rain events

Samples have to be taken during rain events to gain lab measurements over the whole concentration range (high concentrations for the parameter of interest are expected only during CSO events). Due to the difficulty to predict the time arrival of impacts at river monitoring station, only one event have been picked manually during the first two monitoring years. Figure 29 shows samples taken on a regular basis as in Figure 28 and add samples taken during CSO impacts (event on 23 July 2010, black rectangle). A linear correlation exists between spectrometer and lab measurement but no local calibration can be drawn on the basis of only one event. More events are needed to set a reliable calbration function and calculate uncertainties following the same method as sewer monitoring. However, it is interesting to notice that the spectrometer is sensitive enough to the water quality variation.

As the manual approach often fails to catch CSO impacts, the installation of an automatic sampler to pick samples seems necessary to build good calibration functions. Consequently, we purchased an autosampler for the last monitoring year in 2012. The device will start sampling as soon as the COD concentration (from global calibration) reaches a defined threshold, in order to get samples in the upper range.

At the end of the year, the optimal number of events to build accurate calibration functions can be identified, based on a similar approach as for the sewer monitoring (see chapter 5.5).
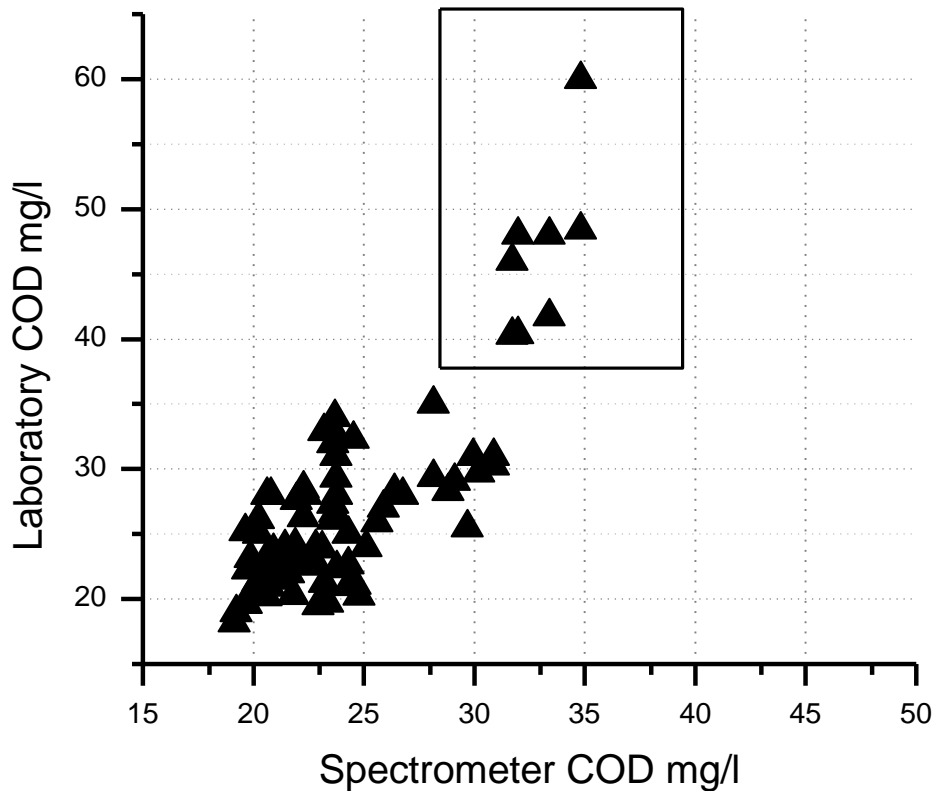
Figure 29. COD lab measurements at station 6 in 2010 and 2011 against spectrometer measurements; samples taken on a regular basis + during rain event (black rectangle).

Ammonium case

In the river Spree, ammonium concentrations are generally pretty low (0-0.4 mg/l). During rain events concentrations can reach 1-2 mg/l. As it is quite difficult to sample precisely at the time of the impact to get NH_4 lab measurement in the upper range, it is recommended to perform monthly NH_4 measurements in a bucket of river water spiked with ammonium standard solution to reach values in the range expected during CSO (1-2 mg/l). The probe should then be immersed in the solution and moved slightly until the voltage signal becomes stable. A sample of the solution is taken and analysed later in the lab and the voltage measurement is written in the "NH_4 sampling protocol" (see appendix C).

5.1.3 Laboratory analysis

Each water sample is carefully documented (see protocol in Appendix D) with the following information: Monitoring station, Date, Time, Sample ID number. Stickers are also filled up with the same information if samples are brought to the lab. These informations are stored later on a laboratory database containing all lab results.

Samples are analysed directly on site for COD, CODd and NH_4 using small tubes tests (from Hach Lange company) to avoid the degradation of COD during transport. Other parameters have to be analysed in the lab of the closest wastewater treatment plant. For the sewer monitoring, samples are stored and cooled between 2 and 4 °C until an operator arrives on site. Samples are then split into two sub-samples, one for the analysis of the parameter on site and one for the lab analysis. This operation should be done carefully as it can be one of the main sources of error. Sample bottles should be well homogenised. 20 cl bottles are used for each sample, used for test cuves measurements and brought to the lab by car.

Analyses are made on site following etablished laboratory protocol and in the lab following reference methods. Analytical errors are reduced by using an electronic pipette. Sample homogenisation is assured by a magnetic stirrer. Each parameter is double checked with two test cuves.

5.2 Calibration of spectrometer with consideration of uncertainties

In order to evaluate the quality and representativity of the measurements, uncertainties are determined at each step of the calculation of pollutant loads. Two main sources of uncertainty have to be considered for both concentration and flow measurements: (i) sensor uncertainties of the probes and (ii) field uncertainties due to the measurement conditions (Métadier and Bertrand-Krajewski, 2011).

5.2.1 Concentrations measurements

For measurements of concentrations, sensor uncertainties derive from

- the intrinsic sensor measurement error (error on x, u(x)). The variance of repeated spectra measurement with a spectrometer under laboratory conditions showed a low average uncertainty of about 3% (Krajewski *et al.*, 2007).

  $u(x) = t_{(0,975, f=n-2)} \bullet s(x) = 3\%$,

  where $t_{(0,975, f=n-2)} \sim 2$ for a high number of observations, $t_{(0,975, f=n-2)}$ student's t-distribution with n-2 degrees of freedom and significance level of 5%.

- the error of laboratory measurement on samples (error on y, $u_{lab}(y)$). Several errors affect the quality of the laboratory results. Main errors come from sampling (pipette, sample representativity), sample storage, sample transport and sample analysis. For example, laboratory COD total uncertainty is estimated to 10% propagating uncertainties of sampling (5%) and lab analysis (5%) (Lombard *et al.*, 2010). $u_{lab}(y) = 10\%$.

Both errors on spectrometer and lab measurement create uncertainties on the coefficients of the calibration regression (slope a and intercept b in the case of linear regression $y = a \cdot x + b$). Uncertainties on these parameters can be easily determined performing Monte-Carlo analysis or analytical calculations.

The Monte-Carlo method is used to perform linear regressions between raw spectrometer measurement and lab values, considering both uncertainties. Regression can be calculated analytically but calculations remain complex if uncertainties on both variables x and y should be accounted for. Ordinary regression method (OLS) should not be applied since it does not allow to consider uncertainties on x variables and makes the hypothesis of a constant variance of y values over the whole range, which is not the case with lab measurement (relative uncertainty of 10% and variable absolute uncertainty better represent nature of chemical analysis). Figure 30 shows an example of calibration regression for COD using the Monte Carlo method.

The Monte-Carlo method analyses the statistical distribution of the regression coefficient, running a high number ($N_{mc}>10000$) of calibration simulations (see Krajewski, 2007). The first step consists in generating N_{mc} data sets of n available data pairs (x_i, y_i) for Monte Carlo simulations. For each spectrometer value x_i, a random sample of N_{mc} values x_{ij} with $j = 1:N_{MC}$ is generated assuming normal distribution of x_{ij} values around the mean value x_i with standard deviation based on the observed intrinsic sensor error $u(x_i)$: $s(x_i) \sim 0.5 \bullet u(x_i)$. The same procedure is applied to generate samples of y_{ij} values based on y_i and the lab error $u_{lab}(y_i)$. For the N_{mc} data sets of n points (x_{ij}, y_{ij}), ordinary least square regression OLS are performed and the parameters a_j and b_j are calculated. The parameters a and b are calculated as the averages of the N_{mc} a_j and b_j. The function $\hat{y} = ax+b$ is then applied to calculate calibrated values from the validated measurements (see data management chapter 4).
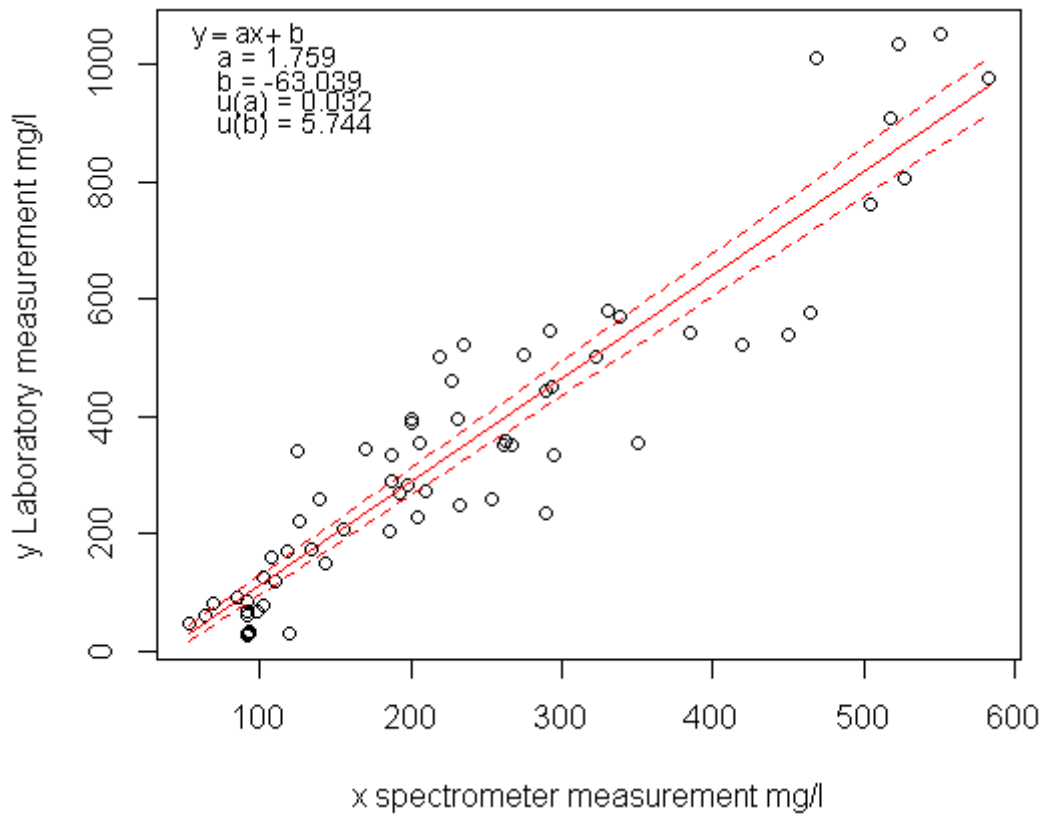
Figure 30. Calibration plot for COD measurement at the sewer monitoring station. 66 lab measurements from 8 events have been analysed and plotted. The dashed curves are the 95% confidence interval of the regression.

Calibration function

$$\hat{y} = a \cdot x + b,$$

with,

- a = average from N_{mc} data sets of a_j
- b = average from N_{mc} data sets of b_j

Confidence interval

The 95% confidence interval contains 95% of the calibration curves from the Monte Carlo simulations. The 95 %-bands are defined by y_{sup} and y_{inf} for each x value:

$$y_{sup} = (a + t_{(0.975,\ f=n-2)} \cdot u(a)) \cdot x + (b + t_{(0.975,\ f=n-2)} \cdot u(b))$$

$$y_{inf} = (a - t_{(0.975,\ f=n-2)} \cdot u(a)) \cdot x + (b - t_{(0.975,\ f=n-2)} \cdot u(b))$$

with,

- $u(a)$ and $u(b)$ standard deviations of N_{mc} data sets of a_j and b_j
- $t_{(0.975,\ f=n-2)} \sim 2$ for a high number of observations, $t_{(0.975,\ f=n-2)}$ student's t-distribution with n-2 degrees of freedom and significance level of 5%

The uncertainty of a point of the calibration function depends on x and is then calculated as

$$u(\hat{y}) = (y_{sup} - y_{inf}) / 2 = 2 \cdot (u(a) \cdot x + u(b))$$

Prediction interval

The true value associated with a new prediction is calculated as

$y = a \cdot x + b + \varepsilon$,   - with ε residual of the prediction $(\hat{y}-y)$

$u(y)^2 = u(\hat{y})^2 + u(\varepsilon)^2$,   - with $u(\varepsilon)^2$ variance of residuals $s(\varepsilon)^2$ of $y = a \cdot x + b$
                                             - without considering covariances between a and b

so for each value x, y can be predicted with the uncertainty u(y):

$y = a \cdot x + b \pm u(y)$ [1]

Field uncertainty and total sensor uncertainty

In addition to the above, field uncertainties have to be considered. They derive from the representativity of the in-situ measurements regarding the observed phenomena. For example, concentrations measured near the river bank are assumed to represent an average concentration of the river section. Similar field uncertainty arises for the sewer monitoring due to the position of the water intake in the sewer and the influence of the pump in the segregation of suspended solids. Field uncertainty is not included in $u_{spectro}(y)$ above, since sensors and lab samples are evaluated at the same place. In the following, these field uncertainties were estimated equal to 10% of the measured value, following the suggestion of Métadier and Bertrand-Krajewski (2011).

Summarizing the above, uncertainty of predicted concentrations y was calculated by:

$u_{conc}(y)^2 = u(y)^2 + u_{field}(y)^2$ [2]

As shown in the next graph, total uncertainty depends on concentration and is about 20% for COD at 1000 mg/l for the sewer monitoring.
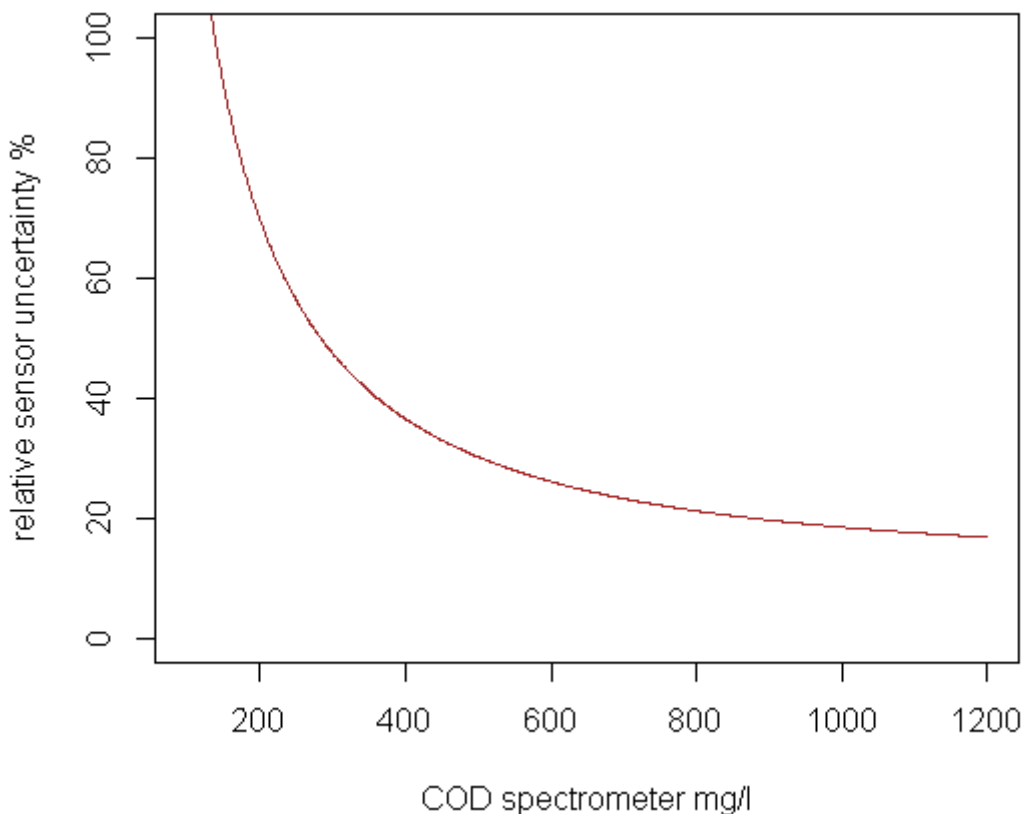

Figure 31. Uncertainty function for COD measurements at the sewer monitoring station

The same analysis has been done for TSS. Total uncertainty depends on concentration and is about 20% at the lab value of 400 mg/l.
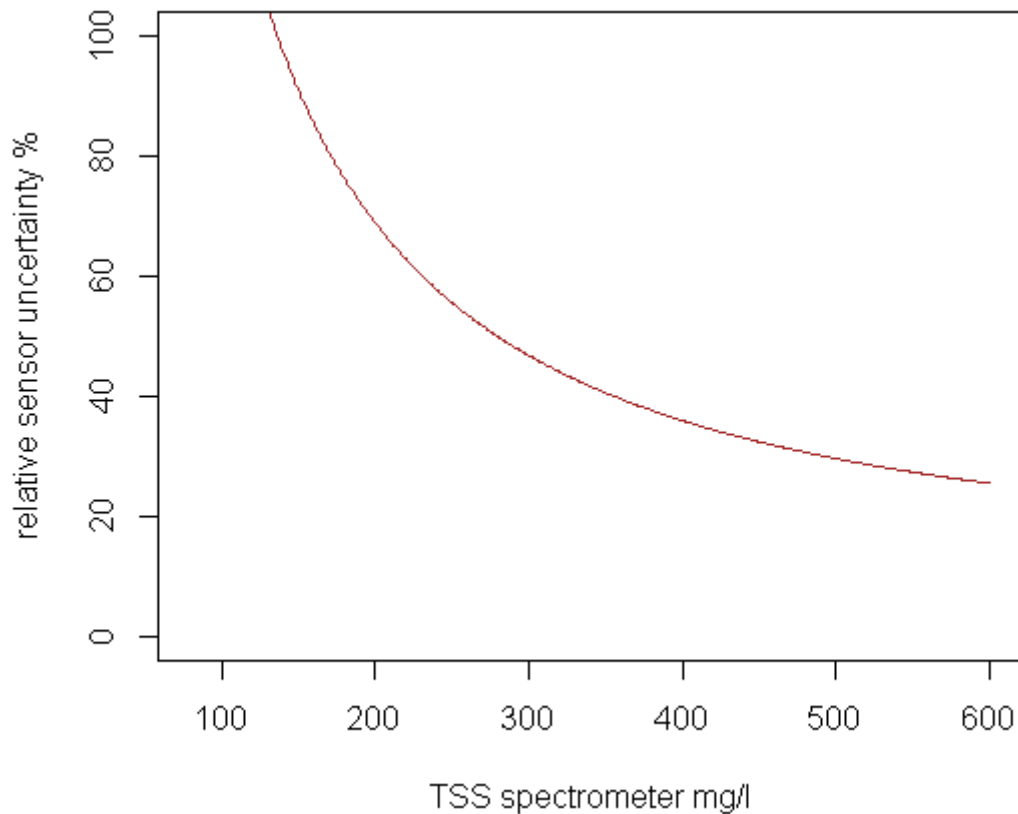

Figure 32. Uncertainty function for TSS measurements at the sewer monitoring station

It is interesting to note that the result is critically depending on intrinsic sensor uncertainty, lab uncertainty and field uncertainty. If intrinsec sensor uncertainty and lab uncertainty have to be defined carefully (variance analysis) field uncertainty remains an assumption and will influence the total uncertainty.

5.2.2 Flow measurements

At the sewer monitoring, flow is calculated as

$$Q = S \cdot v \qquad [3]$$

with,

- v velocity

- S cross-sectional area of water in the sewer

Most of the time, the sewer is completely filled up with water during CSO. In this case, the cross-section used in equation [3] is the cross-section of the entire sewer and uncertainty of level measurements does not need to be considered. Uncertainty on S therefore depends on uncertainties of the cross-section measurement, performed by scuba divers during the installation of the sensors. They measured the width of the sewer at several heights. A Monte-Carlo analysis was run to determine uncertainties of the entire cross-section, based on estimated uncertainties of width and height measurements of 1 cm. Results of the Monte-Carlo calculation give a relative uncertainty of the sewer section of 3.7 %.

Uncertainty of flow speed measurements v were estimated at $u(v)=0.05$ ms^{-1} (empirical function developed by Nivus company). Total uncertainty of the flow $u(Q)$ was calculated at 6% for a velocity of 1 m s^{-1} based on error propagation on [3].
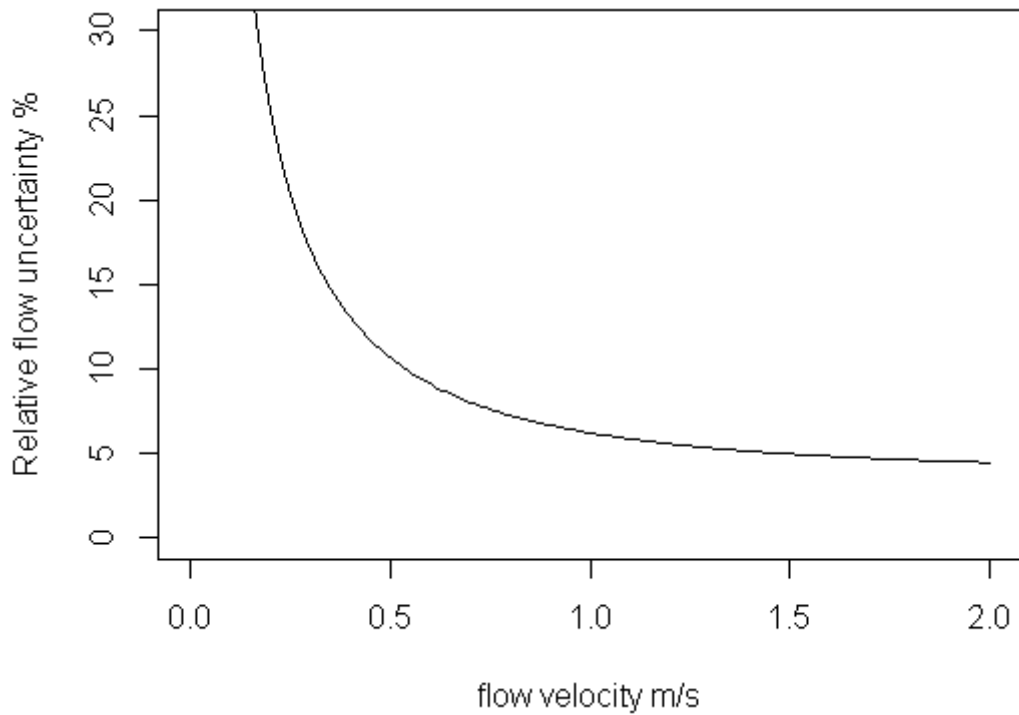
Figure 33. Uncertainty function for flow measurements at the sewer monitoring station

5.2.3 Load calculations

Total uncertainty of loads M was calculated for each time step Δt based on $u_{conc}(y)$ and $u(Q)$ above, again applying the law of error propagation on M:

$$M = \Delta t \bullet y \bullet Q$$

$$u(M)^2 = \Delta t^2 \bullet (u_{conc}(y)^2 \bullet Q^2 + u(Q)^2 \bullet y^2) \qquad [4]$$

Application of [4] leads to significant uncertainties in COD load estimates between 20 % and 70 %. Relative uncertainty is bigger for events with lower loads.

Figure 34. CSO COD load for 8 events in 2011. Error bars show ±u(M).

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5.3 Calibration of ISE Probe (ammo::lyser)

Raw voltage measurement from the ISE-Probe are calibrated to samples of NH_4^+ (calculated from photometric measurements of $NH_{4,tot}$ and pH) using a first order logarithmic relationship $log[NH_4^+] = a \cdot E + b$, simplified from the Nernst equation. This simplified approach assumes that variations in potassium (K), temperature and ionic strength are small within a calibration window.

Sewer monitoring

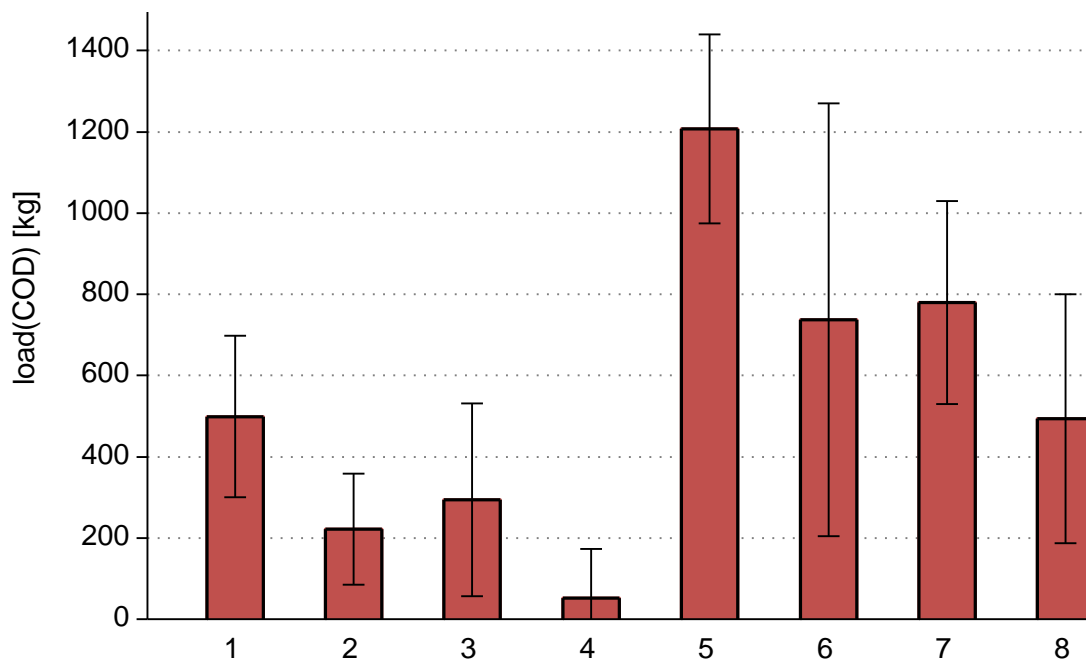For sewer monitoring, a linear calibration has been drawn for 2011. 8 events have been analysed (52 points). Voltage measurement E has been plotted against logarithmic value of concentration $log[NH_4^+]$. Coefficient of correlation R^2 is 0.75.
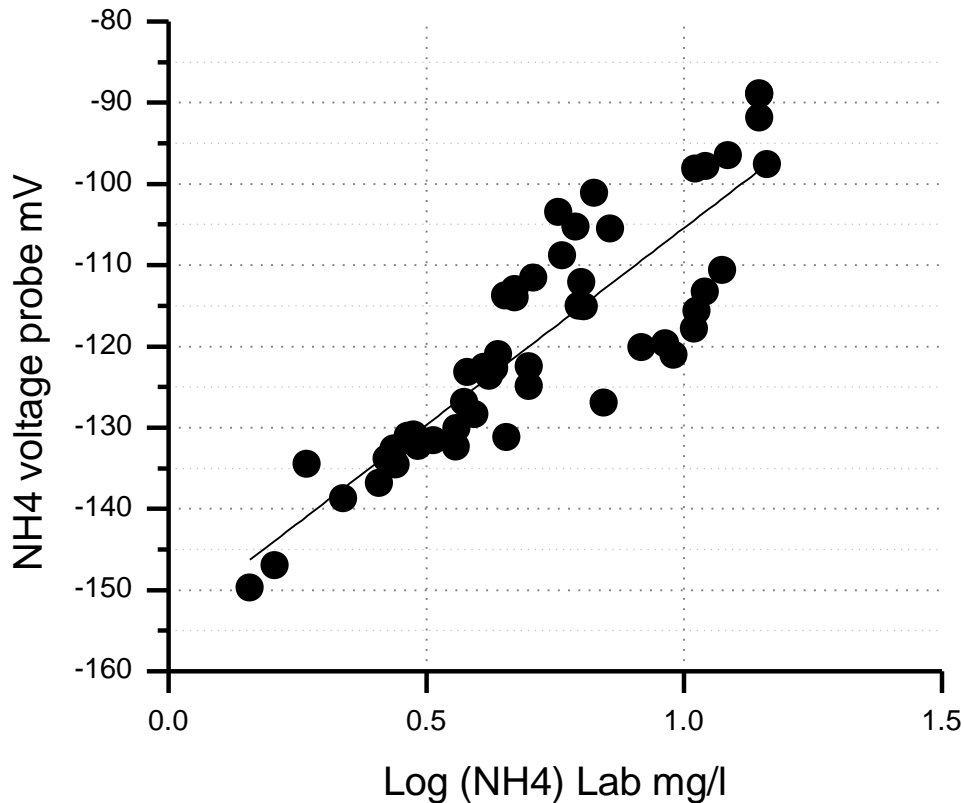
Figure 35. Correlation of voltage values against NH_4^+ lab values; sewer monitoring 2011.

River monitoring

For the river monitoring, calibration windows were chosen to cover periods between several weeks and less than a day, depending on observed drift and variation. NH_4^+ has been calculated from the equation $log[NH_4^+] = a \cdot E + b$. Figure 36 and 37 show one example of calibration construction for the period from 20.04 to 04.05.

Parameter "a" and "b" have been estimated from the regression between voltage measurement and lab measurement for 3 samples within the period (Figure 36). Figure 37 shows an example of calibrated NH_4^+ measurement. The probe is sensitive to NH_4^+ variation and calibrated values fit well with lab values. However, this calibration is valid only during the calibration period: several calibration should be implemented to consider drifts and membrane aging along the year. In our case, 13 calibration periods have been defined between march and october 2011.
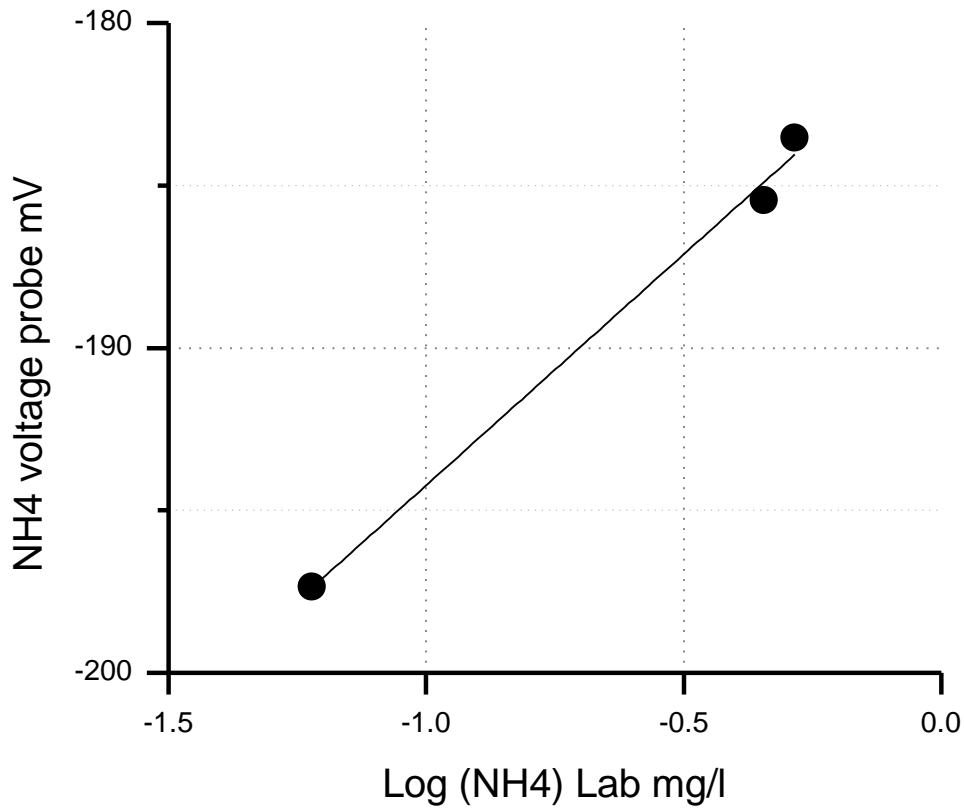
Figure 36. Correlation of voltage values against NH_4^+ lab values; river monitoring station 6, period from 20.04.11 to 04.05.11
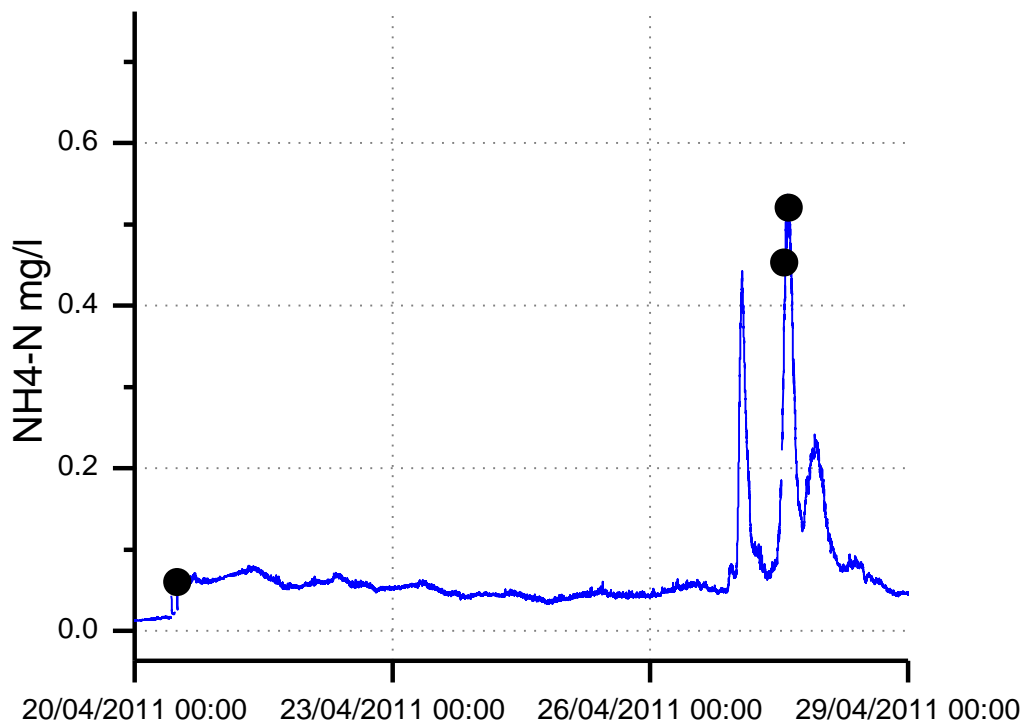

Figure 37. Calibrated NH_4^+ values and lab values used to draw the calibration function.

5.4 Calibration functions implementation

The data logger con::stat allow the construction and application of local calibration functions for spectro::lyser, ammo::lyser and condu::lyser. However, we decided not to use the calibration interface of con::stat online but to define and apply our calibration functions offline. All measurements saved from the probe are calculated with the global calibration. The main reason is that we wanted to save the original raw data from the probe, with a single status and without any correction (see chapter 4 Data management). As it is impossible to know the best local calibration function at the beginning of a monitoring period, using online calibration means changing the calibration function each time new samples are available. It would lead to a confusion about the status of the data, that is to say which correction have been applied to which data.

The second reason is that the calibration interface is quite unclear, especially for NH_4 measurement. No information is given about calculation steps and the weight of correction and compensation factors like pH or Potassium. Furthermore, the voltage measurements between the NH_4 electrode and the reference electrode are quite unstable and are influenced by membrane aging and fouling, even under intensive weekly cleaning. Calculating offline NH_4 concentrations from voltage measurement using a simplified version of the Nernst equation (linear function) and without considering influence of other parameter, worked very well in our case.

5.5 Optimal sampling strategy

5.5.1 Sewer monitoring

For operation purposes, a sewer operator using spectrometer probes to measure water quality would expect to have quality data without the effort of sampling each CSO. In order to estimate the sampling effort required to gain accurately calibrated values, we calculated uncertainty in loads depending on how many events were sampled (or how many lab measurements were done). We simulate all possible random combinations of sampled events (ex: only event1, event2+event3, all events, etc.) and calculate each time the respective measurement uncertainty. 12 events have been analysed in 2010-2011 (83 lab values). For each event between 4 and 14 measurement points are available.

Using the software R, the following steps have been performed:

1. Simulation of all random combination of sampled events (4095 combinations)

2. For each combination i:

- Identification of lab and spectrometer COD measurements.

- Calculation of the coefficient of the calibration curve: linear regression (Ordinary Least Square) between spectrometer and lab measurements (e.g. Figures 38-39).

- Calculation of uncertainty in concentration considering all available measurements (prediction interval at 95%). Uncertainty has been calculated at the spectrometer value of 1000 mg/l, in the upper measurement range.

- Plot of relative uncertainty in concentration in function of number of events used in the combination i (Figure 40).

3. Boxplot of mean error and confidence intervals of the error for each number of events used in the combination (Figure 41).

Figure 38. Calibration curve built with lab values from one event (event 1). The grey line shows the calibration curve built with values from all events.

Figure 38 shows a calibration curve built only with lab measurement of one event. The grey line shows the calibration curve built with all lab measurements. As expected, the grey curve is quite different from the black curve; the correction of raw measurements with this calibration curve would lead to a high underestimation of COD measurement in the upper range, resulting in a high uncertainty of 62 %.

Figure 39 shows a calibration curve built with a random combination of 6 events. As several events have been used to correlate lab and spectrometer values, the calibration is more robust and closer to the one including all events. A calibration with this combination of events would minimise errors on concentrations.
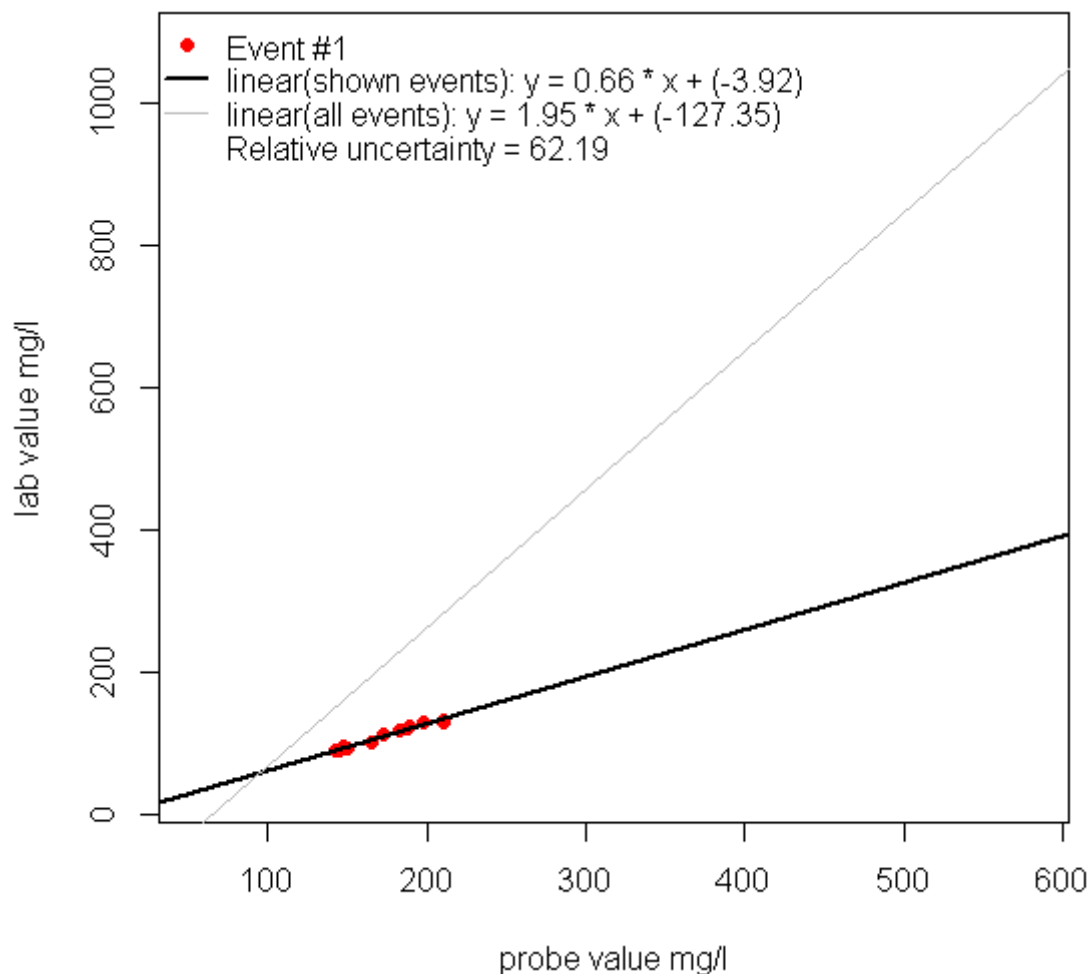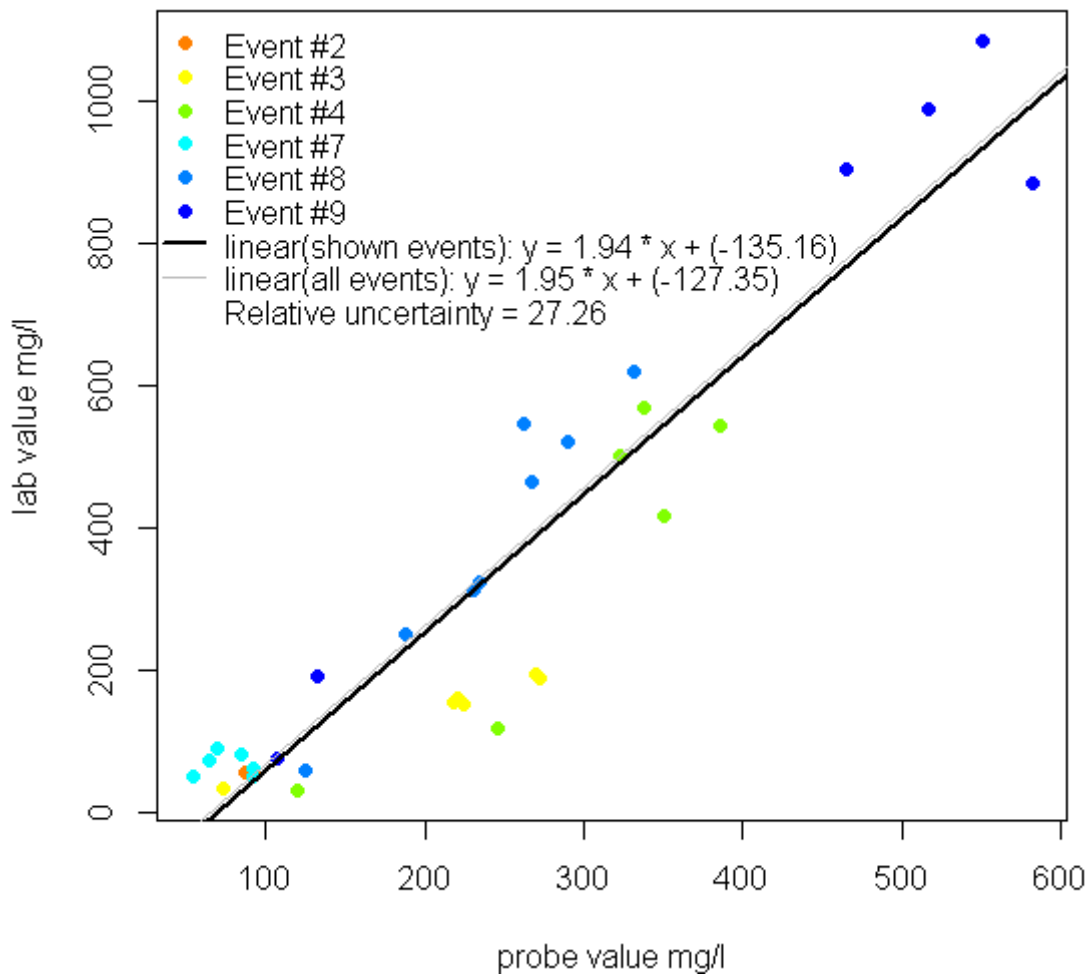
Figure 39. Calibration curve built with lab values from a combination of 6 events. The grey line shows the calibration curve built with values from all events.

To estimate the optimal number of sampled events for a specific uncertainty, the distribution of errors for each number of combination have been analysed (Figures 40 and 41). If very few events are used to create calibration functions the mean error of concentrations are very high. A calibration function built with one single event estimates concentrations with errors between 25 % (if one is very lucky) and more than 100 %. The variance of error decreases with the number of events and the mean error converges toward ± 27 %. According to the graph, the analysis of more than 7 events decreases uncertainties under 30% at 95% probability (see Fig. 41). It means that statistically, at least 7 events should be sampled to reduce concentrations uncertainty under 30% (probability of 95%).
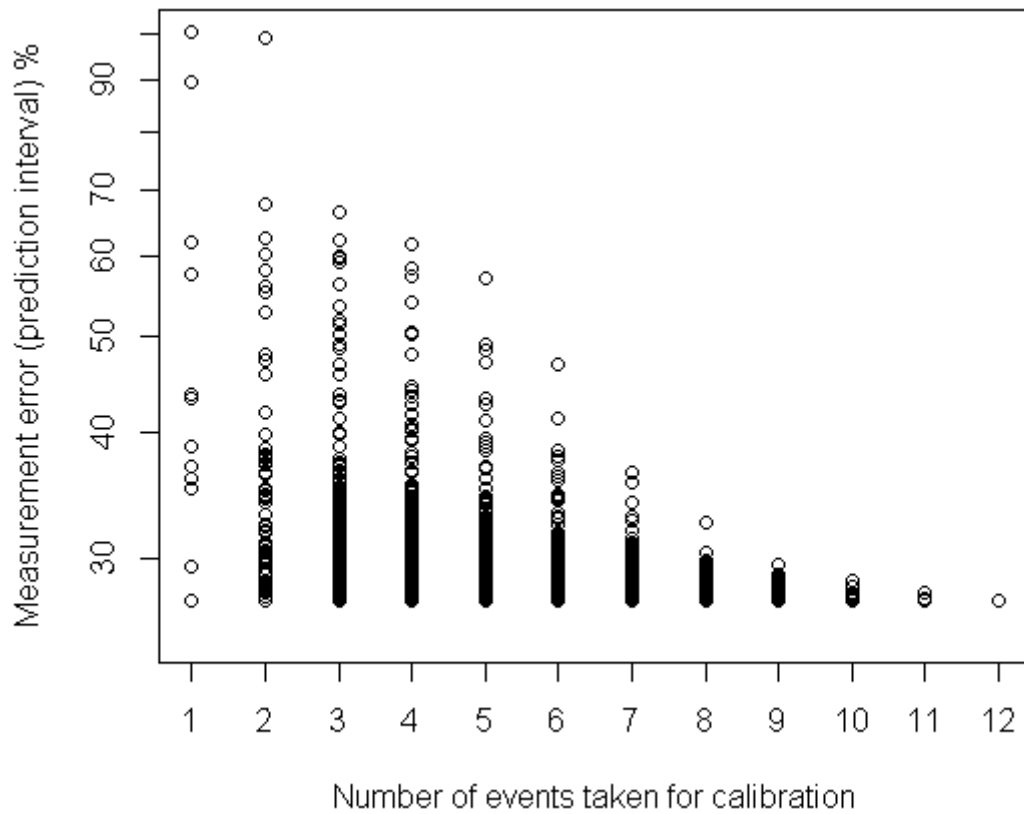
Figure 40.   Relative measurement error according to the different random combinations of events used to build the calibration function.

Figure 41.   Boxplot (line: median; box: 25 and 75 quantiles; whiskers: 5 and 95 % quantiles) of measurement error according to the number of events used to build the calibration function.

In a second step, the influence of the range of the laboratory measurements of each combination of events have been analysed. For each combination i, the difference between the maximal and minimal lab values have been calculated. Figure 42 shows the measurement error as a function of the range of the lab values used for the calibration. The measurement error decreases strongly when the range of the lab values i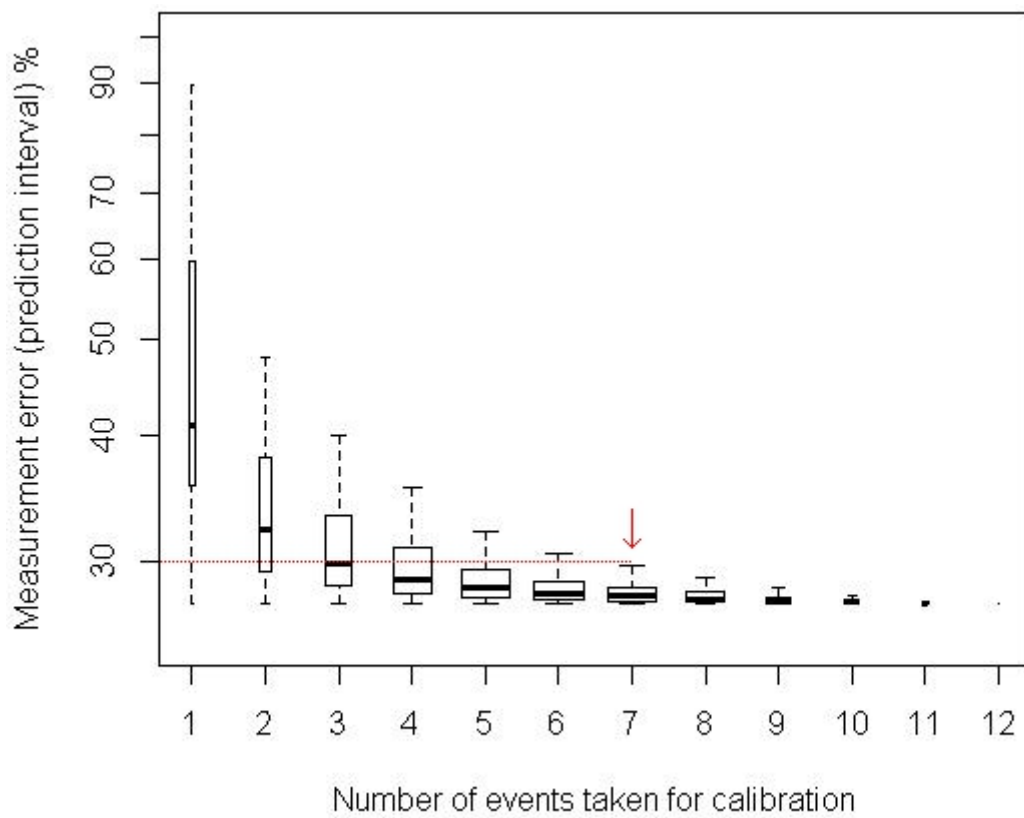ncreases, without any consideration of the number of events. The range of lab values used to build the calibration seems to be a suitable criteria to define good calibration practices. Low error can be reached if the laboratory range covers the entire range of the expected water quality variation.
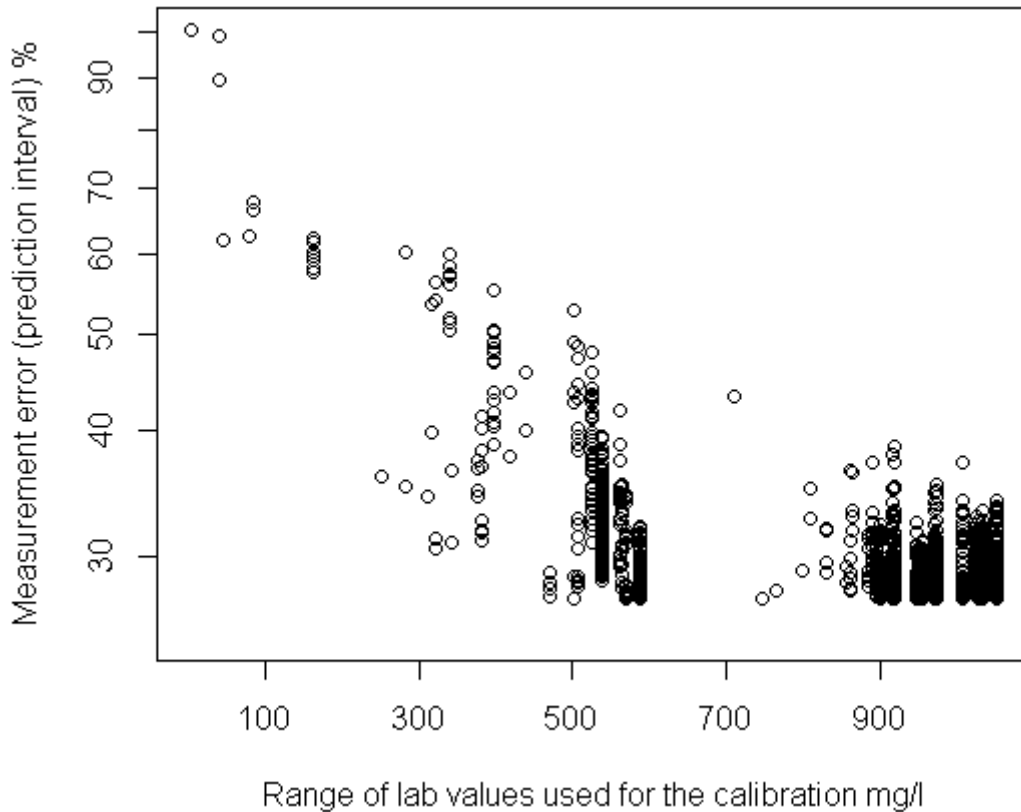
Figure 42. Relative measurement error for each combination in function of the range of the lab values used to set the calibration curve.

In conclusion, the quality of the calibration depends on

- The number of events/points, which are sampled. Uncertainty of less than 30% can be reached if more than 7 events are used for the calibration of the probe (probability of 95%, at the lab value of 1000 mg/l).

- The range of the laboratory values. Without any consideration of the number of events, an acceptable precision can be reached if the range of the laboratory values covers the entire range of water quality variations.

To consider the influence of both factors, we analyse the error distribution for combination of events with high COD ranges only (lab value max. – lab value min. > 500 mg/l) (Figure 43). Only five events with high range are available among the 12 events. According to the graph, a combination of more than 4 events decrease uncertainty under 30%. Combination of 2 or 3 events lead already to uncertainties of less than 35%.
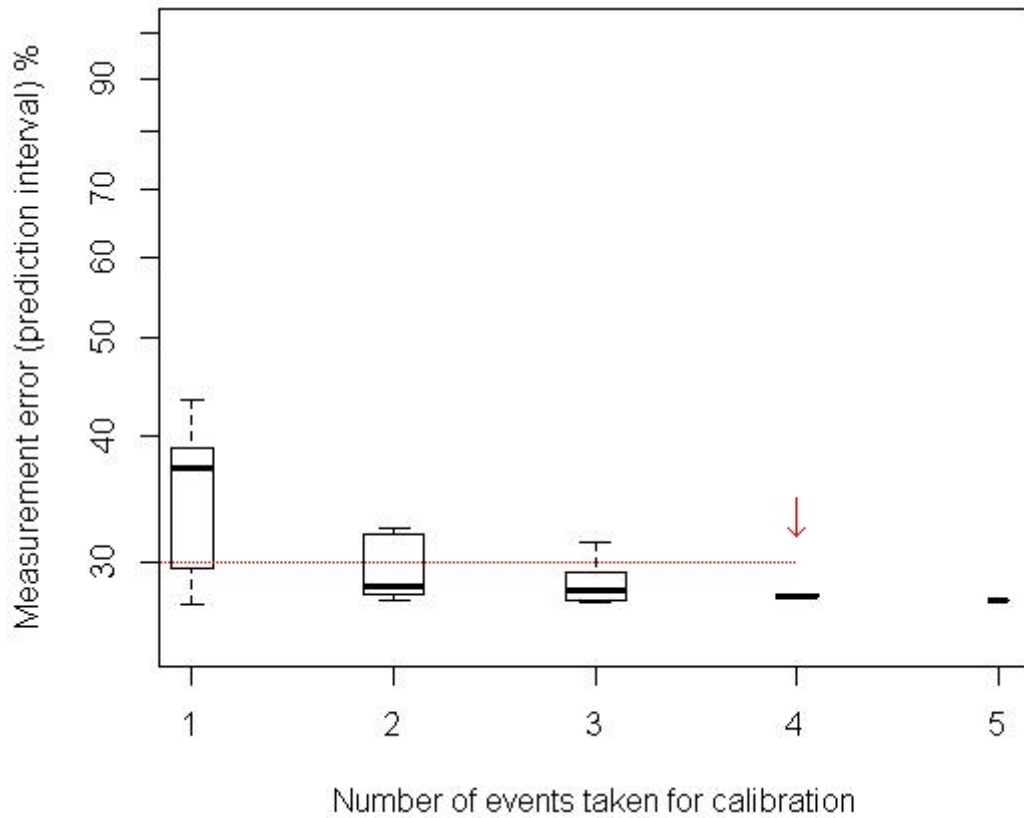
Figure 43. Boxplot (mean; 5,25,75,95 percentile) of measurement error according to the number of events used to build the calibration function. Only combination of events with range>500mg/l are considered.

Considering these results, we recommend for further application of spectrometer for CSO monitoring to lead parallel short sampling campaigns with autosamplers (grab sampling). If the lab measurements cover the entire range of water quality variations, a minimum of 3-4 sampled events should be achieved to build an accurate calibration function with acceptable uncertainties. If later measurements show that the range is larger than expected, additional sampling campaigns will be necessary.

Chapter 6 Measurement of pollutant load in CSO: comparison online sensor and autosampler

Classically, pollutant loads in CSO or rivers are measured by analysis of samples collected using automatic samplers. Explosion-proof autosamplers can be set in the sewer system, triggered by external probes like velocity sensors to start sampling. Grab sampling informs about the temporal variability of pollutant for a specific sample frequency. Limitation to this approach are the high operation costs and the difficulty to get the full variation of concentrations, as combined sewer water quality can vary very quickly.

An alternative solution is the utilisation of online sensors to measure water quality quasi-continuously (in our case at a one-minute time step). This approach enables to get a high temporal resolution of variations in water quality. Limitations are the cost of the devices and the operation effort, even if on the long run the effort could become less than for autosampler operation. A second drawback is the calibration step. Probes need to be calibrated to local conditions to reduce uncertainties and an autosampler is needed anyway to get samples for a set of events (see chapter 5). The local calibration can then be used to measure continuously without the systematic validation of measurements with autosamplers and lab measurements.
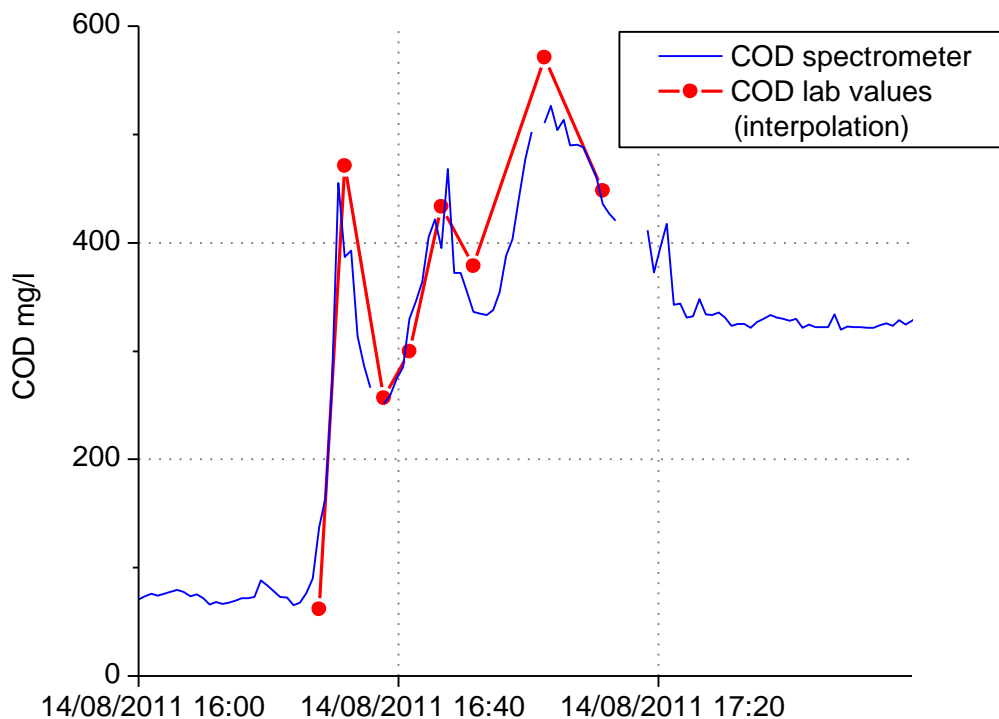
Figure 44. Concentrations from spectrometer and interpolated lab measurements for an event in 08.2011

During the presented monitoring program, water samples have been taken during CSO events in parallel to online sensors (e.g. Figure 44). CSO loads have been calculated with two methods: (i) using online probe measurements (time step =1min), and (ii) lab samples (time step 5 min). To match lab values (time step 5 min) with flow values (time step 1 min), lab values have been interpolated at a time step of 1 min.

Uncertainty of loads based on online measurements have been calculated according to section 5.3. To identify the reliability of both methods to describe pollutant load, load calculated with lab values are compared to the uncertainty band of loads calculated from online probe values (Figure 45). The uncertainty of load based on lab values cannot be calculated since the error due to the interpolation at a time step of 1 min is unknown.
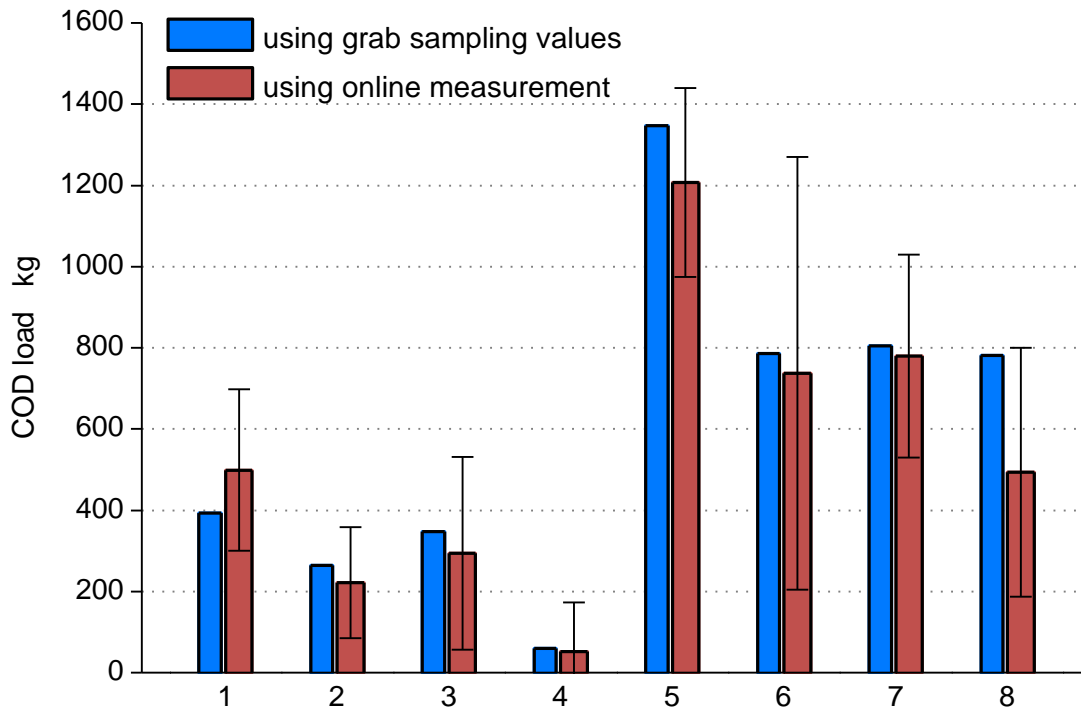
Figure 45. Load calculations from lab and online probe measurements. Boxplot shows load uncertainty (from online probe measurements) as 95% confidence interval.

Results show clearly that loads from lab values are within the confidence band of loads from spectrometer values. For load calculations, autosampler approach seems suitable even for a long term monitoring campaign. Indeed, in our case a sampling frequency of 5 minutes enables to match most of the pollutant variation of CSO and is enough to calculate load with a relative acceptable uncertainty. Table 1 proposes a short overview of advantages and drawbacks of both methods for load calculations.

Autosampler enables to calculate load in the same uncertainty range of online probes with much lower device, operation and calibration costs. However, some types of CSO analysis (first flush, load contribution identification, etc.) requires high resolution data with a time step of less than 5 minutes. For a complete description of CSO, autosampler are limited by their minimal sample frequency and the sampling capacity. Investment and effort of online CSO monitoring seem necessary to overcome these limitations.

Long term CSO monitoring	Spectrometer	Autosampler
Concentration measurement	+++ Full variability	+ Good variability for high grab sample frequency (5 minutes)
Parameter selection	+ Fixed list of parameter	+++ All parameter can be analysed in the lab after sampling
Device costs	- High (~ 20000 €) + autosampler for calibration (~ 4000 €)	++ Low (~ 4000 €)
Monitoring station costs	- High, by-pass or ponton solutions, need for pumps, compressors, etc.	+++ Low, could be hanged in a manhole
Operation and maintenance costs	- High, one operator visits the station each week (2 hours / week). The operator should also come to the station during autosampling campaigns (2 hours / event)	++ Low, one operator comes to the station only after CSO events to get samples (2 hours / event)
Laboratory costs	+ Low, analysis and sample transport costs for several random events	- High, analysis and sample transport costs for each CSO events
Precision / uncertainty for load calculations	+ For CSO monitoring (COD), between 20 and 70%	+ For high frequency sampling, in the uncertainty range of the spectrometer
Reliability	+ Medium, part of the monitoring station could fail during or before the event (ex: pump damage, blockage, etc.)	+ Medium, main failure comes from blockages of the aspiration pipe. Sampling capacity could be exceeded for long duration events (no more bottles available)

Table 1. Overview of main drawbacks and advantages of both online probes and grab sampling methods for CSO load calculation

Conclusions

In 2010, a continuous integrated monitoring, using state-of-the-art online sensors (spectro::lyser, ammo::lyser from s::can company), was started in Berlin. It combines (i) continuous measurements of the quality and flow rates of CSO at one main CSO outlet and (ii) continuous measurements of water quality parameters at five sites within the urban stretch of the receiving river.

This report gathers return on experience and practical aspects gained during two years of monitoring using online sensors. The results show the applicability of online sensors for dynamic measurements of CSO and water quality impacts for a wide range of parameters.

Captured data quality depends firstly on the quality of the raw measurements. A significant handling and maintenance effort is required to avoid disturbances of the measurements: both for the UV/VIS and the ISE probes weekly maintenance was shown to be a prerequisite for high quality data. During the two years operation, the maintenance methods have been continuously improved. Detailed information for each instrument type is available in Appendix A.

Online monitoring produces a high amount of data. Methods have been developed to secure, validate and calibrate the measurements using semi-automatic tools. These tools could be used for further monitoring campaigns and could be easily transferred for operational applications or other monitoring projects (e.g., as already done for odour monitoring project Artnose).

The experience shows that online UV/VIS and ISE probes are not able to provide accurate measurements of water quality without being calibrated to local conditions with laboratory measurement. In the present case of CSO monitoring, samples for laboratory measurements are gained from autosampling campaigns; results are then correlated with in-situ probe measurements. This correlation is both site and probe specific. Total uncertainty of the probe is between 15 and 30% for COD and AFS measurement. Uncertainty of COD CSO load ranges between 20 and 70%, depending on the average concentration and flow of the event.

The analysis of calibration functions indicates that at least 7 random rain events should be sampled to calibrate the probe and reduce uncertainties in COD concentrations under 30%. The concentration range covered by the grab samples also highly influences the quality of the calibration. If the range of the lab measurement for each event corresponds to the entire range of the expected water quality variation at least 4 random events should be sampled to reduce uncertainty under 30%.

Considering these results, we recommend for further application of spectrometer for CSO monitoring to lead parallel short sampling campaigns with autosamplers (grab sampling). If the lab measurements cover the entire range of water quality variations, a minimum of 3-4 sampled events should be achieved to build an accurate calibration function with acceptable uncertainties. If later measurements show that the range is larger than expected, additional sampling campaigns will be necessary.

Load and uncertainty analysis for both spectrometer and grab sampling measurements indicate grab sampling is suitable to calculate CSO loads in the same uncertainty range as with online measurements. However, the frequency of grab sampling needs to be smaller than 10 minutes, to match concentration peaks and quick water quality variation in CSO.

For CSO load calculation, autosamplers remain a cost-effective alternative to online probes. For an extended description of CSO (pollutant sources, mass/flow balance, etc.), the autosampling approach is limited by the minimal sample frequency and the sampling capacity. Investment and effort of online CSO monitoring are necessary to overcome these limitations.

For river monitoring, online probes enable to measure water quality variations with an acceptable uncertainty, if the probes are properly calibrated. However, even under

precautionary operation of the probe, good data quality is not guaranteed especially for river monitoring, where NH_4 range is very small (between 0 and 2 mg/l). Autosamplers are limited by the sampling capacity as the impacts can be spread over several days (in the case of the Berlin River Spree).

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Appendix A: Factsheets instruments CSO monitoring

Online monitoring devices:
description, maintenance, operation

Project: MIA-CSO

Spectro::lyser

Technical data

Name	spectro::lyser™ UV-Vis, s::can
Foto	
Functional principle	Spectrometer probes work according to the principle of UV-VIS spectrometry. Substances contained in the medium to be measured weaken a light beam that moves through this medium. The light beam is emitted by a lamp, and after contact with the medium its intensity is measured by a detector over a range of wave-lengths. The concentration of substances contained determines the size of the absorption of the sample – the higher the concentration of a certain substance, the more it will weaken the light beam. ATEX certification.
Parameter	TSS, TOC, BOD, COD, CODd, NO3…
Spectral range	220 – 720 nm

Maintenance

Action	Optimal frequency / duration	Remark
Automatic cleaning	20-60 min / 10s	Cleaning frequency has to be adapted to local conditions. For sewer monitoring we recommend a frequency of 20 min to avoid measurement drifts. For river monitoring it depends on the set-up solution. If the probe is operated on a pipe-bypass (see Mühlendamm station), we recommend each 20min. For fixation with probe carrier 1h is sufficient. A cleaning pression of 5 bar is recommended.
Manual cleaning	1-2 w / 10 min	The cleaning of the measuring windows is performed using a soft sponge or cotton swabs moistened with water. For the removal of strongly adhering fouling, use s::can cleaning brushes and clean the probe in the following order: • Drinking water • Pure alcohol (Ethanol) • 3% Hydrochloric acid (HCl), availabe in pharmacy You can check the need to use Ethanol and HCl by measuring distilled water in the referencement slide after manual cleaning with water only and after complete

		cleaning. If no change in the readings occurs, a cleaning with water only is sufficient. In our campaign, weekly cleaning with HCl were only necessary for the bypass fitting river monitoring (Mühlendamm). The flow conditions and the plastic bypass fitting could decrease the efficacity of the automatic cleaning and enhance fouling.
		You can check the possibility to decrease the cleaning frequency by measuring distilled water before and after cleaning with water only. If no change occurs in the readings after one week monitoring, you can decide to clean you probe manually every two weeks. However, as water quality can rapidely change in both river and sewer, it is more secure to check and clean the probe every week.
		For bypass fitting, it is very important to clean the inflow and outflow pipes, to avoid fouling and resuspension of solids during automatic air cleaning. In sommer, the operation should be done almost each week, in winter it is not necessary.
Referencement	1-6 months / 20 min	In order to avoid any change in the relation between optic and pollutant parameters, regular referencements are necessary. The measurement of the zero absorbance is checked with distilled water. If a concentration drifts, the offset has to be set to zero.
		Clean the probe but not the measurement windows and measure distilled water into the functionnal slide after rinsing it 3 times. Readings should be 0 for each parameter, if they drift try a complete cleaning of the measurement window and perform a new measurement in distilled water. Considering the readings drift, you can choose to reference the probe or to follow without referencing.
		You can also follow the steps of the con::stat functionnal system check. Main drawback of this procedure is that the values are not displayed before referencing.
		It is recommended at the beginning to check the referencement (system check) each month and to decrease the frequency if referencement are not needed for several months.
		For bypass fitting probes it is quite easy and quick to check referencement (10 min). For other installation type like probe carrier access to the measurement window can be harder and referencement longer (20min). In that case it could be useful to decrease referencement frequency.
		In our case, referencement were checked for both sewer and river probes each 3-4 months.

Condu::lyser

Technical data

Name	Condu::lyser™, s::can
Foto	
Functional principle	The toroidal conductivity sensor consists of two toroids integrated into a tube-shaped housing. The measured medium flows around the housing as well as through the hole localed in the center of the measuring device. One toroid acts as a transmitter and the other as a receiver. Energizing the transmitter toroid induces an electric field in the measured medium which induces an electric current in the receiver toroid. The strength of the induced current is directly proportional to the conductivity of the measured medium.
Parameter	EC, T
Measuring range	0-2 S/cm

Maintenance

Action	Optimal frequency / duration	Remark
Manual cleaning	1-2 w / 5 min	Cleaning frequency has to be adapted to local conditions. A thin layer of fouling will not affect the measurement.
Calibration/Control	2 months / 15 min	We recommend to control EC measurements with certified standard solutions and to perform 2 points calibration if necessary. Temperature should always be calibrated first.

ISE-Probe

Technical data

Name	ammo::lyser™, s::can
Foto	
Functional principle	The combination of a selective membrane with the electrolyte inside the electrode allows the measurement of the redox potential corresponding to one specific ion (for example NH4 +). When such an ion selective electrode is combined with a reference electrode a voltage is measured that can be converted into a substance specific concentration using the Nernst equation. Total concentration of dissolved ammonium is calculated considering pH and T influence. Because of the similarity of potassium ions with ammonium ions (e.g. size, charge), the ion selective membrane of the ammonium electrode is also partially permeable to potassium ions. As a result, the presence of potassium in a sample will result an overestimation of ammonium concentrations when only an ammonium selective electrode is used. By also measuring potassium online, compensation for the contribution of potassium to the ammonium concentration is possible.
Parameter	NH4-N, K, pH, T
Measuring range	NH_4-N: 0,1 – 20 mg/L pH: 2 – 12

Maintenance

Action	Optimal frequency / duration	Remark
Automatic cleaning	1h / 10 s	Pressure should not exceed 2,5 bar.
Manual cleaning	1 w / 15 min	The probe should be cleaned with a soft sponge, cloth or brush using medium water. In the case of sewer monitoring, the probe can be cleaned with drinking water. Resistant fouling can be treated with a 3% aqueous solution of hydrochloric acid (HCl). The probe should be replace immediately in the medium after cleaning.
Calibration/control T	2 months / 15min	Adjustment of the temperature calibration is best performed in-situ against a suitable reference thermometer. The temperature sensor is the only one that can also be calibrated on air.

Calibration/control pH	2 months / 15 min	2 points pH calibration should be performed in standard buffer solutions covering the whole range of the pH variations. As the pH compensation of the NH4 concentration is especially relevant around pH 8, at least one calibration standard in the alkaline range (pH > 7) should be used.
Membrane replacement	6 months / 30 min	For river monitoring, NH4 and K membranes should be replace each 6 month. For sewer monitoring, membranes should be replace each year. A new electrolyte is filled into the electrode during the replacement. Do not tilt the tool for membrane replacement when screwing and unscrewing the membrane cap because the electrode head can break off. To avoid drifts we recommend to change the membrane in both monitoring every 6 months.
Electrode replacement	2 years	Only reference and pH electrodes.

Con::stat

Technical data
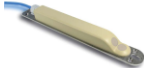
Name	Con::stat™, s::can
Foto	
Function	The s::can con::stat is an industrial computer for on-line operation of submersible s::can probes. It ensures communication with the measuring devices as well as the visualisation, transmission and storage of the data measured. It controls also the opening of the automatic cleaning valves.

Maintenance

Action	Optimal frequency / duration	Remark
Control dessicant cartridge	1 month / 1 min	To avoid malfunctions due to condensing humidity, a desiccant cartridge has been built into the housing cover. When the cartridge has reached the maximum humidity absorption capacity, it has to be exchanged to prevent the formation of dew on the internal components in low temperatures.

Velocity sensor / Level sensor / Flow data logger

Technical data

Name	Flow velocity sensor, Nivus
Foto	
Function	Flow velocity sensor using cross correlation and temperature measurement to compensate the temperature effect on the velocity of sound
Parameter	T, v
Measurement range	-1 to 6 m/s

Name	Level measurement sensor, Nivus
Foto	
Function	The ultrasonic sensor sends ultrasonic impulses in the direction of the medium. The medium to be measured will reflect these sonic impulses as echoes and transmits this signal to the transmitter. The distance is calculated from the sonic transit time.
Parameter	H
Measurement range	0.3 – 6 m

Name	OCM Pro CF, Nivus
Foto	
Function	Data logger and display for water level and flow velocity sensors. Flow calculation.
Parameter	H
Measurement range	0.3 – 6 m

Peristaltic pump

Technical data

Name	P_classicplus, Ponndorf
Foto	
Functional principle	Peristaltic pump
Max. aspiration height	8 m

Maintenance

Action	Optimal frequency / duration	Remark
Greasing	2 weeks / 10 min	The flexible tube must always be covered of a grease film.
Flexible tube change	4 months / 1 hour	It is highly recommended to change the flexible tube of the pump at least each 4 months to avoid tube break. If the tube becomes untight, waste (or river) water flows in the pump body. It could damage the rotor bearing and decrease the pump capacity.
Pump cleaning	/	In case of pump flexible tube break, the pump inside could be in contact with contamined water. The pump should be dismounted and cleaned, to avoid fouling and accumulation of solids in the rotor bearing.

Appendix B: Risk and safety information

Vorhandene Gefährdungen

Die Gefahren im Container können folgenden Ursachen zuschreiben: durch Gase und Dämpfe, Vergiftungsgefahr, Explosionsgefahr, Infektionsgefahr.

Gefahren durch Gase und Dämpfe:

Beispiele besonderer Gefahren durch Gase und Dämpfe in umschlossenen Räumen von abwassertechnischen Anlagen

In umschlossenen Räumen von abwassertechnischen Anlagen können Flüssigkeiten, Gase und Dämpfe durch unzulässige Einleitungen oder in Störfällen eingebracht werden oder infolge von chemischen bzw. biologischen Reaktionen entstehen. Durch das Vorhandensein dieser Stoffe können Gefahren drohen. In der Regel handelt es sich um Gefahren durch:

Sauerstoffmangel (O_2-Mangel)

Alle zusätzlich eingebrachten Gase und Dämpfe reduzieren den Sauerstoffanteil in der Atmosphäre der u. R. a. A..

Konzentration von O_2 in der Luft	Symptom/Wirkung
20,9 Vol.-%	Konzentration in der unbelasteten Frischluft
< 18 Vol.-%	Gesundheitsschädlich
< 10 Vol.-%	Unter 10 Vol.-% Sauerstoff schwindet das Bewusstsein ohne Warnung. Gehirnschädigung und Tod folgen in wenigen Minuten, wenn nicht sofort eine Wiederbelebung erfolgen kann.

Benzindämpfe

Alle Dämpfe brennbarer Flüssigkeiten sind schwerer als Luft.

Konzentration von Benzindämpfen in der Luft	Symptom/Wirkung
~ 0,6 Vol.-%	Untere Explosionsgrenze (UEG)
~ 8 Vol.-%	Obere Explosionsgrenze (OEG)
500 bis 1 000 ppm	Reizung der Atemwege, Kopfschmerz, Schwindelgefühl, Übelkeit, Konfusion bis zur Bewusstlosigkeit

Kohlenstoffdioxid (CO_2)

Kohlendioxid ist schwerer als Luft.

Konzentration von CO_2 in der Luft	Symptom/Wirkung
0,03 Vol.-%	Anteil in der unbelasteten Frischluft
0,07 Vol.-%	Stadtluft
0,1 – 0,3 Vol.-%	Hohe Werte in Büroräumen
0,5 Vol.-%/5 000 ppm	Arbeitsplatzgrenzwert (AGW)

Konzentration von CO_2 in der Luft	Symptom/Wirkung
ca. 1 – 4 Vol.-%	Reizung der Schleimhäute; Atembeschleunigung; Blutdruckanstieg; Erregung; Herzklopfen; Kopfschmerzen
ca. 5 – 9 Vol.-%	Kopfschmerzen, Ohrensausen (Tinnitus), Herzklopfen, Blutdruckanstieg, psychische Erregung, Schwindel, Benommenheit
> 9 Vol.-%	Bewußtlosigkeit nach 5 – 10 Minuten Einatemdauer
Über 10 Vol.-%	Lähmung des Atemzentrums; Narkose; Tod

Methan (CH_4)

Methan ist leichter als Luft.

Konzentration von CH_4 in der Luft	Symptom/Wirkung
4,4 Vol.-%	Untere Explosionsgrenze (UEG)
17 Vol.-%	Obere Explosionsgrenze (OEG)

Schwefelwasserstoff (H_2S)

Konzentration von H_2S in der Luft in ppm	Symptom/Wirkung
0,003 – 0,02	Geruchliche Wahrnehmbarkeit
3 – 10	deutlich unangenehmer Geruch
20 – 30	starker Geruch nach faulen Eiern
5	Arbeitsplatzgrenzwert
50 – 100	Reizungen des Atemtraktes
100 – 200	Verlust des Geruchssinns
250 – 500	Toxisches Lungenödem, Zyanose, Bluthusten, Lungenentzündung
500	Kopfschmerzen, unkoordinierte Bewegungen, Schwindelgefühl, Stimulation der Atmung, Gedächtnisschwäche, Bewusstlosigkeit („knockdown")
500 – 1 000	Atemstillstand, sofortiger Kollaps, schwerste Nervenschädigungen, arhythmische Herztätigkeit, Tod

Explosionsgefahr

In dem Regenüberlaufkanal in der Stallstr. gilt die Explosionsschutzzone 2. Im Container selbst gilt daher die Explosionsschutzzone 3.

Gefahren durch biologische Arbeitsstoffe

Biologische Arbeitsstoffe können bei Menschen Krankheiten auslösen, Voraussetzung dafür ist, dass der jeweilige Krankheitserreger in den Körper gelangt. Verschiedene Aufnahmewege sind möglich:

Durch den Mund
- durch Spritzer
- durch verunreinigte Nahrungsmittel
- durch Essen, Trinken und Rauchen oder Schnupfen ohne vorherige Reinigung der Hände
- durch jeglichen Hand-Mund-Kontakt

Über die Haut oder Schleimhäute
- Durch Eindringen bei Hautverletzungen
- Durch Nässe aufgeweichte Haut
- Durch Schmutzspritzer in die Augen und Nase
- Bei verhinderter Schutzbarriere der Haut durch Ekzeme
- Durch alle Hand-Gesicht-Kontakte

Eindringen in tiefes Gewebe bei Verletzungen

Folgende biologische Arbeitsstoffe sind nach derzeitigem Stand im Abwasserbereich hinsichtlich einer Gefährdung der Gesundheit zu berücksichtigen:

Viren
Sechs Erreger stehen im Vordergrund: Das Hepatitis-A-Virus, das Hepatitis-B-Virus, das HIV, das polio-Virus und stellvertretend für die „Durchfallviren" das Rota- und das Norwalk-Virus.

Das Rota-Virus und Norwalk-Virus verursachen Durchfallerkrankungen. Die relativ hohe Durchseuchung von Berufsanfängern lässt eine hohe Infektiosität vermuten. In der Regel handelt es sich um keine schweren und durch hygienmaßnahmen vermeidbare Erkrankungen.

Das Polio-Virus kann über Ausscheidungen in das Abwasser gelangen und dort relativ lange überleben. Das Risiko ist bei 1-3 gemeldeten Fällen pro Jahr in der Gesamtbevölkerung gering. Jedoch in Zeiten einer polio-Epidemie ist ein deutlicher Anstieg der Gefährdung für Beschäftigte anzunehmen.

Einige wissenschaftliche Studien zeigen, dass Beschäftigte in der Kanal- bzw. Kläranlagenunterhaltung gegenüber der Allgemeinbevölkerung häufiger Antikörper gegen Hepatitis A im Blut besitzen. Hieraus wird indirekt ein erhöhtes Risiko für die genannten Bereiche geschlossen. Für Kanal- und Rohrleitungsbauer, die in der Regel nur sporadisch Abwasserkontakt haben, lässt sich kein derartiges Risiko nachweisen. Es besteht wohl nur ein geringes Risiko, beim Umgang mit Abwasser an Hepatitis A zu erkranken. Die meisten Hepatits A Infektionen verlaufen ohne Symptome, bei älteren Beschäftigten sind jedoch schwerwiegende Krankeitsverläufe möglich.

Eine Infektion an Hepatitis B erfolgt in der Regel nur dann, wenn das Virus direkt oder über Haut- bzw. Schleimhautläsionen in die Blutbahn gelangt, nicht aber durch Aufnahme über den Mund oder über die intakte Haut. Ein besonderes Infektionsrisiko wird als nicht vorhanden angesehen.

Eine HIV Infektion durch Abwasser erscheint derzeit als äußerst unwahrscheinlich. Es wird dadurch begründet, dass eine sehr große Viruszahl für eine Infektion notwendig ist, die aber im Abwasser wegen des Verdünnungseffektes praktisch nicht erreicht wird, und das Virus außerdem in einer körperfremden Umgebung sehr instabil ist.

Bakterien

Die Leptospiren sind ernst zu nehmen. Sie werden durch Ratteurin übertragen und können in aufgeweichte oder verletzte Haut eindringen. Die Leptospirose ist selten, kann aber schwer verlaufen. Sie ist gekennzeichnet durch untypische Symptome und mit grippalen Infekten leicht zu verwechseln. In der Literatur sind immer wieder Fälle im Zusammenhang mit dem Abwasserbereich beschrieben worden. In Deutschland gibt es 15-20 Fälle pro Jahr (aus Meldestatistik und nicht in Zusammenhang mit abwassertechnischen Anlagen), das Erkrankungsrisiko ist zahlenmäßig als gering einzuschätzen.

Darmerkrankungen wurden zu Beginn einer Beschäftigung oder nach längerer Abwesenheit der Mitarbeiter beobachtet, sie sind vermutlich auf Infektionen durch E.coli Bakterien, Rota-Viren und Norwalk-Viren zurückzuführen.

Pilze
Pilze können Infektionskrankheiten verursachen oder allergische Reaktionen auslösen. Da humanpathogene Pilze im Abwasser keine optimalen Wachstumsbedingungen antreffen, kann eine gesundheitliche Beeinträchtigung durch Pilze vernachlässigt werden.

Durch allgemeine Hygienemaßnahmen kann die Zahl der Schmierinfektionen verringert werden

Sicherheitsvorkehrungen

Impfschutz

Den Empfehlungen der ständigen Impfkommission (STIKO) am Robert Koch-Institut ist zu folgen. Sie sind im Epidemiologisches Bulletin vom Robert Koch Institut, 27. Juli 2009/Nr. 30 zu finden.

-   Der Impfstatus gegen bestimmte Infektionskrankheiten sollte regelmäßig überprüft werden.
-   Die Impfung gegen Hepatitis A (HA) wird empfohlen für Kanalisations- und Klärwerksarbeiter mit Abwasserkontakt.

Stellen Sie sicher, dass Ihr Impfstatus überprüft ist!

Es wird empfohlen, sich gegen Hepatitis A zu impfen. Sofern die Kosten für diese Impfung von Ihrer Krankenkasse nicht übernommen werden, werden sie vom Kompetenz Zentrum Wasser Berlin gGmbH beglichen.

Sicherheitsvorkehrung am Container

Beim Betreten des Containers sind feste Schuhe zu tragen.

Das Hängeschloss wieder abriegeln, um im Container nicht eingesperrt zu werden!

Ein Gaswarngerät ist während der Arbeit am Container mitzuführen (Gefahr Entweichen von Schwefelwasserstoff, Explosionsgefahr durch Entweichen von Faulgas (Methan), Sauerstoffmangel).

Der Container muss vor dem Betreten gelüftet werden.

Vor Beginn der Arbeiten empfiehlt sich die Anwendung von Hautschutzmittel (Desinfektionsmittel wirken auf den natürlichen Schutzfilm der Haut ein und können bei unsachgemäßer Anwendung zu Hautschäden führen).

Für die Analyse des Wassers aus dem Bypass sowie für die Reinigung des Bypasses und der Messgeräte sind Schutzhandschuhe, eine Schutzbrille und eine Kittel zu tragen.

Das Trinken, Essen oder Rauchen im Container ist verboten.

Vor den Pausen und nach der Arbeiten sind die Hände zu waschen und zu desinfizieren. Die Verwendung von Hautschutzmittel wird empfohlen.

Der Kontakt mit Wasser aus dem Bypass ist zu vermeiden.

Im Störungs- oder Notfall

Werden schädliche Gase festgestellt (Geruch, Dämpfe, Alarm der Gasmessgeräte), darf der Container nicht betreten werden bzw. ist der Container sofort zu verlassen.

Bei defekten elektrischen Betriebsmitteln ist die Elektroinstallation ausschließlich durch Elektrofachkräfte instand setzen zu lassen.

Bei Brand: Ein Feuerlöscher ist unter dem Schreibtisch installiert, die Feuerwehr anrufen. Wenn ein Brand sich ausbreitet, kein Risiko eingehen und den Container schnell verlassen. Nicht versuchen, die Geräte zu retten! Wenn möglich, Tür schließen. Entfernt bleiben von dem Container bis zur Ankunft der Hilfeleistung.

Bei Personenschäden Erste Hilfe leisten, Rettungsdienst verständigen und ggf. Unfallarzt aufsuchen.

Bei Kontakt mit Mischwasser oder Lösungen aus den Küvetten-Tests:

- Kontakt mit der Haut: zuerst mit Wasser und Seife reinigen, schließlich vorgesehenes Desinfektionsmittel benutzen.

- Kontakt mit den Augen: sofort mit Augenspüllösung reinigen und schnell einen Augenarzt aufsuchen.

Beim Überlaufen des Messtopfes: Der Strom im Stromkasten ist auszuschalten, Container reinigen, wenn notwendig mit Entsorgungsdienst der BWB. Vor Wiedereinschalten des Stroms ist zu überprüfen, dass keine Steckdose vom Wasser belastet worden ist.

Reference:

Deutsche Gesetzliche Unfallversicherung, Arbeiten im umschlossenen Räumen von abwassertechnischen Anlagen, BGR 126, aktualisierte Fassung September 2008

Notfallnummern

Feuerwehr/ Rettungsdienst: 112
Polizei/Notruf: 110

Augenarzt in der Nähe der Stallstraße:
Dr. med. Benedikt Camps
Adresse: Kaiser-Friedrich-Str. 46
10627 Berlin
Tel.: (030) 324 48 34

Im Vandalismusfall rufen Sie die folgenden Telefonnummern an:
Polizei-Notruf: 110
nächste Polizeiwache:
Adresse: Abschnitt 24, Kaiserdamm 1
14057 Berlin
Tel.: (030) 4664 - 22 47 00

Kontakt-Nr. am KWB:
Andreas Matzinger: 030 5365 3824
Pascale Rouault : 030 5365 3816
Monika Jäckh: 030 5365 3840
Nicolas Caradot: 030 5365 3805

Kontakt Kanalbetrieb der BWB in Ruhleben:
030 8644 3805 (Herr Siewert)
030 8644 3848 (Herr Reichert)
030 8644 3850 (Herr Rustig)

Hiermit bestätige ich, dass ich eine Einweisung für die Arbeiten im Container erhalten habe. Ich bin über die Gefahren und die Sicherheitsvorkehrungen informiert und habe sie verstanden. Ich verpflichte mich, mich daran zu halten. Die Einweisung muss ein Mal pro Jahr wiederholt werden.

Datum, Unterschrift   Datum, Unterschrift
                                                           Unterweisende(r)

Appendix C: NH4 sampling protocol

Probenahmestelle　　　8664 Stall.　　　　　　　　8665 Teg.　　　　　　　　8666 Mühl.　　　　　　　　Datum

	NH4	K	NH4 mV	K mV	KT NH4	KT NH4	KT K	KT K	ID Nr. / Uhrzeit	NH4 Neue Kali?	K Neue Kali?
Vor R.											
N R.											
Eimer											

Probenahmestelle　　　8664 Stall.　　　　　　　　8665 Teg.　　　　　　　　8666 Mühl.　　　　　　　　Datum

	NH4	K	NH4 mV	K mV	KT NH4	KT NH4	KT K	KT K	ID Nr. / Uhrzeit	NH4 Neue Kali?	K Neue Kali?
Vor R.											
N R.											
Eimer											

Appendix D: Spectrometer sampling protocol

Probenahmestelle	8664 Stall.	8665 Teg.	8666 Mühl.

Sample ID		Probename	

Datum		Uhrzeit (WZ)	

Ergebnisse KT		**Sonde**	
CSB	CSB	CSB	
CSBf	CSBf	CSBf	
P	P		
PO4	PO4		
NH4	NH4	NH4	NH4mV
K	K	K	KmV

BWB-Laborprobe	AFS BSB TOC	Ja / Nein
	NO2 NO3 TKN	Ja / Nein