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VALIDATION OF AN INTEGRATED ROBOTIC PLATFORM FOR IN-SITU QUALITY MONITORING OF SURFACE WATER

Master thesis

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Abbreviations

AAS	atomic absorption spectrometry
ATU	allyl-thio-urea
BOD ₅	Biochemical Oxygen Demand in 5 days
CO ₂	Carbon dioxide
COD	Chemical Oxygen Demand
C _{org.}	organic carbon
DO	Dissolved Oxygen
EC	Electric Conductivity
FI	bottle volume
FLUO	fluorescence spectrometry
GPS	Global Positioning System
ICP	atomic emission spectrometry
INTCATCH	Integrated Tools for Monitoring and Managing Catchments
IR	InfraRed
ISA	In-Situ Spectrum Analyzer
Na ₂ CO ₃	sodium carbonate
NaOH	sodium hydroxide
NH ₄	Ammonium
NO ₂	Nitrite

NO ₃	Nitrate
O ₂	Oxygen
PO ₄	Phosphate
TOC	Total organic carbon
TSS	Total suspended solids
Turb	Turbidity
UV	Ultraviolet
VIS	Visual
WFD	Water Framework Directive
WLAN	Wireless Local Area Network
$C_6H_8O_6$	Ascorbic acid
H_2MoO_4	Molybdic acid
H_2O	Water
H_2PO_4	Dihydrogen phosphate
$H_3P(Mo_3O_{10})_4$	Phosphomolybdic Acid
$K_2Cr_2O_7$	Potassium dichromate

Abstract

The monitoring of water quality is challenged with providing the limit for safeguarding the protection of the environment from harmful biological effects of anthropogenic chemical pollution from diffuse and point sources. To meet this challenge, the European Union has taken the first steps with the promotion of the Water Framework Directive (WFD). With it, one goal of the WFD is the improved monitoring of water quality to measure quality problems faster and more effectively. Nowadays measurement needs a lot of time because of a high workload for each parameter. This leads the European Union to launch the project "INTCATCH". The participating project partners come from six different countries from universities and companies. Their task is to monitor the quality of surface water with new ways. Both the parameters of the Quality Target Ordinance Chemistry - Surface Waters and those of eutrophication must be observed. The necessary classification of this system can be carried out with validation according to the international standard. Tests are carried out which simulate the real state as well as possible. Particular attention is paid to the measurement of the parameters for determining the eutrophication since these measurements can only be measured around the year 2017 with online monitoring. Another challenge is to test the functionality of the system (boat). Communication skills play a major role here since everything had to work so that clear recording was possible. The system turned out to be very good except for a few small details, and the measurement of the eutrophication parameters showed good results. In the future, this form of measurement will be widely used because it ensures excellent continuous monitoring of surface waters.

Kurzfassung

Die Überwachung der Wasserqualität ist mit der Festlegung der Grenze für den Schutz der Umwelt vor schädlichen biologischen Auswirkungen der anthropogenen chemischen Verschmutzung durch diffuse und punktuelle Quellen verbunden. Um dieser Herausforderung zu begegnen, hat die Europäische Union mit der Förderung der Wasserrahmenrichtlinie (WRRL) die ersten Schritte unternommen. Ein Ziel der WRRL ist dabei die verbesserte Überwachung der Wasserqualität, um Qualitätsprobleme schneller und effektiver messen zu können. Heutzutage benötigt die Messung aufgrund der hohen Arbeitsbelastung für jeden Parameter viel Zeit. Dies veranlasst die Europäische Union, das Projekt „INTCATCH“ zu starten. Die teilnehmenden Projektpartner kommen aus sechs verschiedenen Ländern von Universitäten und Unternehmen. Ihre Aufgabe ist es, die Qualität des Oberflächenwassers mit neuen Wegen zu überwachen. Sowohl die Parameter der Qualitätszielverordnung Chemie - Oberflächengewässer als auch die der Eutrophierung sind zu beachten. Die notwendige Klassifizierung dieses Systems kann mit Validierung nach dem internationalen Standard durchgeführt werden. Es werden Tests durchgeführt, die den realen Zustand so gut wie möglich simulieren. Besonderes Augenmerk wird auf die Messung der Parameter zur Bestimmung der Eutrophierung gelegt, da diese Werte erst rund um das Jahr 2017 mit Online-Überwachung gemessen werden können. Eine weitere Herausforderung besteht darin, die Funktionalität des Systems (Boot) zu testen. Kommunikationsfähigkeiten spielen hier eine große Rolle, da alles funktionieren musste, damit eine klare Aufzeichnung möglich ist. Bis auf ein paar kleine Details erwies sich das System als sehr gut, dabei zeigte die Messung der Eutrophierungsparameter gute Ergebnisse. In Zukunft wird diese Messform weit verbreitet sein, da sie eine hervorragende kontinuierliche Überwachung der Oberflächengewässer gewährleistet.

1. Introduction

Increased human activities have adversely impacted the surface water quality in the world's watersheds and rivers (Telci, et al., 2009). For this reason, the European Union has sent out an amendment with the Water Framework Directive so that by 2027 all watersheds have a good ecological and chemical status (Helm, et al., 2016). Eutrophication has also become an ever-increasing problem (van der Kolk, et al., 1995) as it can cause harmful algal blooms in surface waters (Ulen, et al., 2007). The eutrophication would be a natural process that takes place slowly and evenly due to leaching from the soil into rivers (Dahanayaka, et al., 2016). But the anthropogenic process leads to an increase in a very short time. Signs of this pollution are increased levels of nutrients like ammonia and phosphorus. It is therefore important that they are fully assessed using monitoring systems (Copetti, et al., 2016). But short-term measurements can no longer take on this pollution monitoring task, they take too long give only a snapshot of the task and cannot show a necessary trend (Rieger, et al., 2008). The best way to visualize these trends is to collect data with high frequency (e.g. hourly or more) with online measuring devices (Etheridge, et al., 2014). Measuring all parameters will increase the capability for appropriate control of surface waters to prevent unnoticed discharges, which harm the ecological condition. (Rieger, et al., 2004). The online monitoring will reduce the effort and also the costs. So the primary purpose of the water quality monitoring system is to generate sufficient information and configure an alarm based on abnormal changes in surface waters to support and enable decision making (Telci, et al., 2009; Girolimon, et al., not dated). It is the only way to identify the source of pollution and/or to oblige potential polluters to start immediate clean-up operations.

As part of the project described in this work, monitoring systems were developed, which enable in-situ, multi-parameter monitoring through combination of several single probes. The main focus is put on detection of wastewater discharges into surface water (Altenburger, et al., 2015). New methods, which should make continuous measurements possible, were used especially for the detection of nutrients such as ammonia and phosphorus (Brighty, 2017). One of these technologies is the UV-VIS spectrometry which is already proved for the detection of compounds like nitrate, chemical oxygen demand

or total organic carbon without chemical manipulations (Sakamoto, et al., 2009). But new developments are performed to measure nutrients, like nitrogen (as ammonium) and phosphorous (as phosphate) using this technology (Go-Systemelektronik GmbH, 2019).

In this thesis, the validation of an autonomous system for in-situ quality monitoring of surface water is described. It includes the evaluation of capabilities of the system under investigation regarding its suitability to detect ammonium and phosphate pollution in surface waters. The validation process consists of indoor and outdoor trials which are performed within a period of four months at the facilities of the Department of Water Atmosphere, Environment at the University of Natural Resources and Life Sciences, Vienna (BOKU).

The thesis is divided into 6 chapters. Chapter 1 gives a brief introduction of why the system should be used. In the second one, the objectives of this work are presented. In the third, the fundamentals of the monitoring principles are described. Chapter 4 contains the practical methodology of the work as well as the material used. The results, which are written in Chapter 5 summarize and discuss the outcome of the experiments. At the end of the main part of this thesis is chapter 6 where the work's conclusion is given, and an outlook is presented. The last paragraphs include a summary, the references of the thesis, bonus material in the appendix, the curriculum of the author and the affirmation of this work.

2. Objectives

The main objective of this thesis is the validation of the boat as an integrated system and its performance to detect contamination and more precisely wastewater.

The first step of this integrated system validation was the calibration of each sensor used on that boat in indoor trials. The second step was the validation of the functionality of the complete platform made with out in outdoor trials. Based on this, the following specific objectives were formulated:

1. What is the effort required for the calibration of the sensors?

During the indoor measurements in the laboratory, various calibrations were created so that the differences between the measurements could be represented so that the best is used for the validation.

2. How robust are the calibrations of the sensors in relation to other water matrices?

It is known that there is a calibration for the system which is used to get local data to achieve the best results after a measurement. It should be tested if the change of the water source is a problem for the use of the system.

3. How the validation process has to be carried out so that the field conditions are adequately described?

The possible situations are simulated in indoor and outdoor trials to reproduce the most accurate possible reconstruction of field conditions in which the system is used. The result is a table that describes the performance of the sensors.

4. Is it possible to measure parameters describing eutrophication with an on-line UV/VIS – Spectrometer?

One of the newest possibilities on the market is the measurement of eutrophication parameters with UV/VIS – Spectroscopy. In this validation these functions were tested.

5. Is the integrated system capable to detect wastewater spills?

This question can be answered by the validation of the whole system with all the performance characteristics.

3. Fundamentals

3.1 Monitoring of water quality

The purpose of water quality control is to obtain quantitative information on the physical, chemical and biological properties of water by statistical sampling (Surface Water Quality Monitoring, 2008). The information sought depends on the goals of the monitoring program. The objectives range from detecting breaches of drinking water standards to determining the state of the environment and to analysing the temporal evolution of water quality (Tousova, et al., 2017). Three types of monitoring can be distinguished: (1) routine monitoring of surface waters, (2) periodic special investigations and (3) special investigations to assess the extent of a pollution problem (e.g.: an investigation of the presence of wastewater in surface waters). The state of water quality is the result of complex natural and artificial conditions and the resulting interactions in space and time (Kornfeind, et al., 2017). As a result, it is often very difficult to abstract the essence of water quality conditions. In practice, water pollution caused by oxidizable substances is often characterized by sum-parameters (Kurzweil, et al., 2012). The monitoring and assessment of the environmental status of European surface waters are carried out by a large number of local, regional and national authorities (Water Framework Directive, 2000). Due to a large number of organizational structures at the national and local level in European countries, the administrative structures for the monitoring activities are very different. Because of the extensive national monitoring of surface water quality as an important source of information, it is important to know the main components of the organizational structure concerned, such as the organizations involved and their responsibilities, the general principles of coordination for monitoring, storage of data, notification of information, etc.

Monitoring

Any attempt to evaluate water quality monitoring programs should answer the question: "Why are we monitoring?" It is very important to be able to describe the goals and objectives of the monitoring as they provide the context for the corresponding monitoring activities, i.e. the construction of the sampling networks, the variables to be measured, the sampling frequency, data storage and use of information, including analysis and data

reports (Pérez, et al., 2017). It can be seen that the direction and magnitude the influences from outside into the rivers is very uncertain due to the insufficient sampling (Gardner, et al., 2006). The purpose of the monitoring is generally defined by legislation or other regulatory measures (guidelines, water quality standards, action plans) and, as described in the previous section, aims to assess the status of the aquatic environment and to identify trends.

Legal measures set targets or standards for water quality (e.g. 50% reduction of nitrogen load in surface waters, no pesticides in drinking water, etc.) (Water Framework Directive, 2000). The objective of monitoring is to provide data and information on water quality related to these regulatory measures (Surface Water Quality Monitoring, 2008).

Many monitoring programs have several goals. One-way monitoring programs can be used in the adoption of new legislation and other aspects of water pollution. Besides, new approaches to water quality management can be considered and thus expanded to collect data and additional information. The goals described above represent one dimension of the monitoring system. Another dimension is associated with activities regarding data collection and the use of information. These activities start with sampling and end with informing the public about the results and the implementation of measures to improve the environmental status of the water body.

The data collection can be described by the monitoring sampling network, the sampling frequency and the measured water quality quantities. By using the information gained, data analysis and notification process can be performed. The following describes these activities.

Network design

The monitoring network will be primarily depending on water (i.e.: springs, brooks, streams, rivers, river systems, ponds, lakes, reservoirs, fjords, estuaries, coastal area, or open marine water) and the geographical area (e.g.: land, river systems, etc.) it covers. However, more detailed information on the selection criteria for sampling points is often needed to evaluate the information obtained from a monitoring program such as the Kriging-based Models or Genetic Algorithms (Karamouz, et al., 2007).

Two types of networks can be identified: (1) a wide-area network with numerous sampling points, a few annual samples, the analysis of specific variables or only one or few years of sampling; (2) a dense network of sampling sites with detailed investigations, numerous

annual sampling or measurements of many variables and long-term observations. Many monitoring networks are both intensive and extensive, such as a subnet consisting of many large samples with few variables, and a subnet that contains relatively few sites with frequent sampling and multiple variables. The river sampling networks should be described according to the sampling site selection strategy, for example, main country flows or frequent sampling from downstream point sources (Surface Water Quality Monitoring, 2008).

3.2 Parameters for measuring water quality

The number of parameters describing the quality of a water body has increased and is constantly changing and evolving. The increasing use of water and the development of analysis options have contributed to the fact that more and more substances are needed to be measured for even lower values of the concentration. Several water user groups have developed their approaches and methods for describing and measuring water quality. Watershed management and control of water pollution have for many decades been based on aggregate variables such as biochemical oxygen demand in 5 days (BOD₅) and chemical oxygen demand (COD) to quantify sewage discharge and oxygen problems in rivers. The measurement of the concentrations of ammonium and phosphorus can also provide quantitative information on the discharge of wastewater. For human consumption and public water supply, several microbiological indicator organisms (e.g.: coliform faecal bacteria) have been identified and their list is now widely used to determine the hygienic appropriateness of drinking water. The variables of water quality can be divided into the following major categories (Surface Water Quality Monitoring, 2008):

- Basic variables (e.g. water temperature, pH, conductivity, dissolved oxygen, and discharge) used for a general characterization of water quality.
- Suspended particulate matter (e.g. suspended solids, turbidity, and organic matter).
- Organic pollution indicators (e.g. dissolved oxygen, Biochemical Oxygen Demand in 5 days (BOD₅), Chemical Oxygen Demand (COD), ammonium).

- Indicators of eutrophication: nutrients (e.g. nitrogen and phosphorus), and various biological effect variables (e.g. chlorophyll a, Secchi disc transparency, phytoplankton, zoobenthos).
- Indicators of acidification (e.g. pH, alkalinity, conductivity, sulphate, nitrate, aluminium, phytoplankton and diatom sampling)
- Specific major ions (e.g. chloride, sulphate, sodium, potassium, calcium and magnesium) as essential factors in determining the suitability of water for most uses (e.g. public water supply, livestock watering and crop irrigation)
- Metals (e.g. cadmium, mercury, copper, and zinc)
- Organic micropollutants such as pesticides and the numerous chemical substances used in industrial processes (e.g. PCB, HCH, PAH).
- Indicators of radioactivity (e.g. total alpha and beta activity, ^{137}Cs , ^{90}Sr)
- Microbiological indicator organism (e.g. total coliforms, faecal coliforms and faecal streptococci bacteria)
- Biological indicators of the environmental state of the ecosystem (e.g. phytoplankton, zooplankton, zoobenthos, fish, macrophytes and birds and animals related to surface waters).

Eutrophication

Eutrophication is a major problem of water quality in surface waters around the world and is mainly caused by contamination of water catchment areas with nitrogen or phosphorus (Fink, et al., 2018). These nitrogenous and phosphate-containing pollutants promote the growth of plants in surface waters due to a large increase in nutrients (Seilnacht, 2019). These fertilizing algal blooms consume oxygen and create hypoxic or dead areas in which only a few can survive (Richard Damania, 2019). The sources of these pollutants vary from fertilization in agriculture to domestic wastewater (Senra-Ferreiro, et al., 2011; Ling, et al., 2011). To slow down this process, monitoring of surface water in increasing population density- and soil sealing areas (more than 10 hectares per day) requires increased control (Galler, 2008). Consequently, to develop strategies to reduce eutrophication, we need a good understanding of the amount, sources and trends of phosphorus pollution (Fink, et al., 2018).

One of these strategies is defined in the Austrian law for Quality target regulation of ecology in surface waters (Bundesministerium für Land- und Forstwirtschaft, 2009), which

is based on the water framework directive. The aim of this regulation is to determine the target states to be achieved and the relevant states for the prohibition of the deterioration of surface water types by values of the biological, hydromorphological and general conditions of the physico-chemical quality components in order to assess the quality of the surface water. The target values of orthophosphate depend on the biological region of the surface water and the trophic degree which contains the size of the catchment area and elevation. In the case of this thesis the aquatic bioregion for the Danube is the “Eastern flat and hilly country” and the trophic degree “meso-eutrophic 2”. This leads to a value of 0,2 mg/l for a good and 0.07 mg/l for a very good state (Bundesministerium für Land- und Forstwirtschaft, 2009).

For ammonium, the determination is a little bit different, the value is dependent on the pH and the Temperature and is calculated by this formula:

$$UQN\ N - NH_4 \left[\frac{\mu g}{l} \right] = \left(\frac{14.425}{1 + 10^{7.688 - pH}} + \frac{621.75}{1 + 10^{pH - 7.688}} \right) * \min (2.85, 1.45 * 10^{0.028 * (25 - T)})$$

Equation 1

This equation was derived from fish toxicity experiments. The value is decreasing with increasing pH - and Temperature value. Usually it is in the range of 0.5mg/l (Konheisner, et al., 2019).

Additionally, the all measurements have tolerance limits where the measurement should work to be used as an online monitoring device. These are shown in Table 1 (Bundesministerium für Land- und Forstwirtschaft, 2009)

Table 1: Tolerance limits for the measured parameters of the system

Parameter	tolerance limits
BOD ₅ [mg O ₂ /l]	4 - 6
COD [mg O ₂ /l]	7 - 10
NH ₄ [mg/l]	0.4 - 0.6
NO ₃ [mg/l]	4 - 7
PO ₄ [mg/l]	0.07 - 0.2
TOC [mg/l]	3 - 4
Turbidity [NTU]	5 - 50
EC [μS/cm]	100 - 1000
pH []	6 - 9
DO [mg/l]	8 - 12

3.3 Online water quality monitoring

As described, the main purpose of the monitoring is generally defined by legislation or other regulatory measures (guidelines, water quality standards, action plans) and aims to assess the status of the environment and to identify trends. The easiest and most comfortable way to ensure this is online-monitoring which should allow short-term variability and long-term trends (Daniel, et al., 2020). That is because this method brings several benefits:

- nearly-continuous and real-time monitoring or instant detection of contamination or to achieve seasonal trends (Jones, et al., 2011).
- elimination of possible changes in the sample during transport, storage and pre-treatment are necessary to get good results.
- data is stored on a server with geo-reference to have the opportunity to mark every measurement on a map for editing a measurement project. The information that is gained with in-situ monitoring can be used to get a detailed plan of the ecosystem (temporary and spatially) and of concentration gradients and transfers the interfaces (sediment-water, water - air, etc.). These data can then be directly broadcasted to any environmental agency (Allabashi, 2018).

- it can be performed at points where sampling is difficult or impossible, there this monitoring practice is very useful (Fleischmann, et al., 2001).
- cost-minimization by reducing analysing costs and sampling time.

To achieve these advantages, the measurement must also be brought to a level that enables real-time monitoring. That this is possible the measurement must consist of three main activities; (1) processing; (2) data analysis and (3) data determination (Telci, et al., 2009). For this purpose, a procedure had to be developed, which differs from the conventional measurement in the laboratory and which eliminates the need for periodically water analyses (Tuna, et al., 2013).

INTCATCH approach

The overall goal of the research project INTCATCH (Integrated Tools for Monitoring and Managing Catchments) is to develop new approaches to monitor and manage the quality of rivers and lakes between 2020 and 2050, especially in the context of the Water Framework Directive (WFD) (Water Framework Directive, 2000).

The Water Framework Directive requires an integrated approach to the monitoring and evaluation of surface water quality (Brighty, 2017). However, the frequency of existing monitoring programs established in each Member State is in the best case monthly and for certain pollutants or programmes every 3 to 12 months. Currently, it is recognized that traditional approaches, including monitoring, operations and survey monitoring, have the following limitations:

- Sampling events are usually "singular", at a specific time and / or within a specific time interval (weekly / monthly).
- The sampling programme is planned and virtually independent of the weather or other variables (except that no samples may be taken).
- The temporary nature of the sampling, with days / weeks in between, where no sampling is performed, and no information can be obtained
- Spatial limitation of sampling to fixed points, without evaluation between locations
- The considerable costs of sampling, transport, analysis and reporting

These limitations of the current 'sampling and laboratory analysis' approach can be overcome. The novel approach to river and lake monitoring and management in the INTCATCH project will conduct an in situ real-time monitoring to understand situations and identify specific contamination events, leading to a better understanding of the

catchment area. The main requirements and functions of the INTCATCH tools are identified as follows (Allabashi, 2017):

- to be able to identify 'event-driven' pollution and wastewater spills
- to be deployed in the field for appropriate periods
- to identify areas where hazards can be readily pin-pointed
- to record data on an on-going basis, and can geo-position the data captured
- to provide greater spatial and temporal resolution than infrequent (monthly) spot sampling
- to engage the community / stakeholder on measurement programmes
- to reduce costs coming from sampling, sample transport and lab analysis
- to support immediate interventions and communications to stakeholders
- to perform an event-triggered sampling in a defined time
- to increase the evidence base to make it compelling to the broadest set of stakeholders

However, the INTCATCH tools support the operational and investigative monitoring of the Water Framework Directive. Investigative monitoring, for example, is used in case of accidents, in case of emerging monitoring, when ecological and chemical status does not match (Allabashi, 2017). They will not be able to replace the current WFD monitoring programs, in particular chemical status compliance (priority substances, etc.). However, INTCATCH is advocating a new method of monitoring surface waters with autonomous robotic boats, sensors and other tools. Their use for investigative monitoring and targeting priority areas for improvement actions envisaged in the project. To meet this challenge, stable signal values are crucial (Allabashi, 2017). The pursuit of differences in water quality or the distinction between "clean" and "temperate" waters is still an informative and useful piece of information that INTCATCH seeks to provide from the perspective of a catchment manager.

The established autonomous robotic system is a platform where pH, Dissolved Oxygen, Electrical Conductivity and spectrometry are combined. The pH value is measured with a glass electrode, at which a potential is measured (Kurzweil, et al., 2012). For Dissolved Oxygen two measurement principles can be usually used, the amperometric and the optical one. In the amperometric method, a current is measured which is created because of the reduction of oxygen. With optical measurement, the measurement is carried out

with the help of fluorescent radiation. The electrical conductivity can also be measured using two methods, the conductive and inductive measurements. The conducting process uses current and voltage flow to determine the value. In comparison, the inductive method measures the conductivity via a voltage which is induced through water from one coil to another. The spectrometry and more precisely UV / VIS spectrometry is a very promising method to evaluate rapid changes in water quality (Langergraber, et al., 2006) using ultraviolet and visible light to measure absorption. It is a simple technique, which can provide a quick analysis (Bi, et al., 2015) and can be used as qualitative and quantitative method (Leong, et al., 2018) as described in the following chapter.

Also, a distinction must be made between two measurement approaches, which can be classified as (1) measurement of surface water at a measuring point near the river shore; (2) direct measurement in the river using: boats, buoys, etc.

3.4 Principles of UV/VIS-Spectroscopy

The UV-VIS spectroscopy measures the specific absorption of samples at a wavelength of 200-400 (UV) and 400-750nm (visible) shown in Figure 1: Electromagnetic radiation Figure 1 (Thomas, et al., 2017).

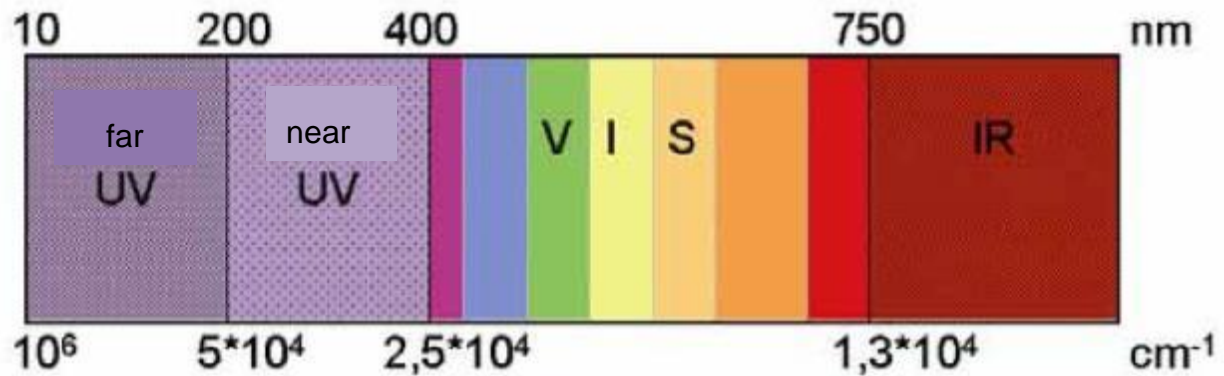


Figure 1: Electromagnetic radiation (Analytik Jena, 2009)

The application range is from monitoring drinking water to wastewater treatment plant monitoring (van den Broeke, et al., 2008). It can also be used for the determination of phosphate or nitrogen compounds in water samples (Pena-Pereira, et al., 2011; Stawicka, et al., 2019). It is known that the emission of electromagnetic radiation is related to the energy levels of the electron shells in atoms (Löffler-Mang, 2012). With the extinction of electrons, in atoms and molecules through the absorption of visible and ultraviolet radiation, the energy level is rising of a lower to a higher level (Royal Society of Chemistry, 2009). However, only light with the right amount of energy can cause a transition from one energy state to another to be absorbed described in Figure 2.

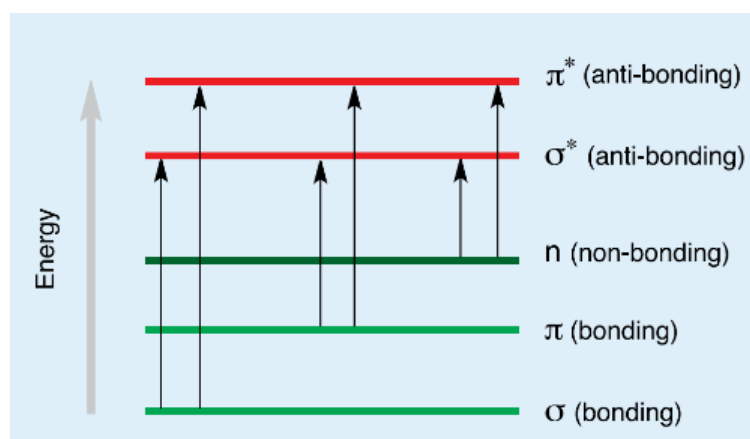


Figure 2: Transition from one to another energy level (Royal Society of Chemistry, 2009)

Electrons can be excited from a full (low energy, ground state) orbit into an empty (higher energy, excited state) anti-bonding orbital (Basic UV-VIS Theory, Concepts and Applications, 2008). If now each wavelength has a particular energy which is associated with it, the electrons will make its transitions just right on one of this wavelength where the radiation is absorbed (Etheridge, et al., 2014).

When the gap between the energy levels gets bigger, the energy to provide the electrons to a higher energy level is higher. This results in a higher frequency and therefore, a lower wavelength, which is absorbed (Royal Society of Chemistry, 2009).

With this knowledge, we can detect a lot of molecules or atoms in a spectrum.

Figure 3 describes the Absorption spectrum and where the specific molecules absorb the radiation, e.g., nitrate at a wavelength of 200 - 250nm or Turbidity at 625 – 700nm (Huebsch, et al., 2015).

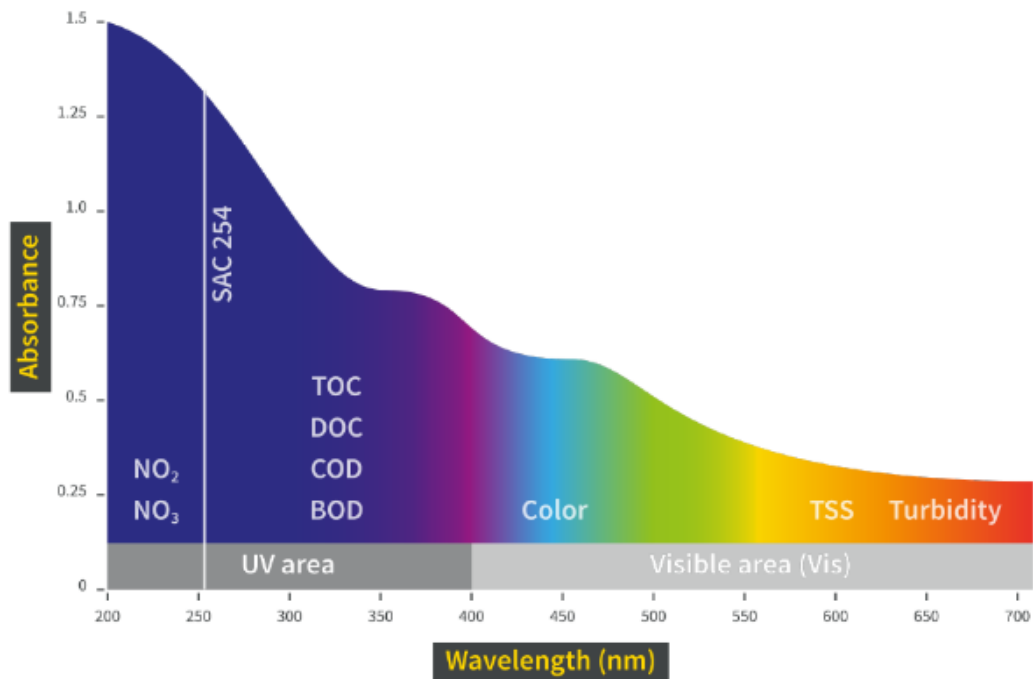


Figure 3: Absorption spectrum (Go-Systemtechnik GmbH)

Technology of analysis

A UV / VIS spectrometer requires a light source that can emit wavelengths of 190-800nm. Deuterium lamps (UV) and tungsten lamps (VIS) have been used in the past. This technology was replaced by xenon lamps that emit electromagnetic radiation both in the UV and in the VIS range.

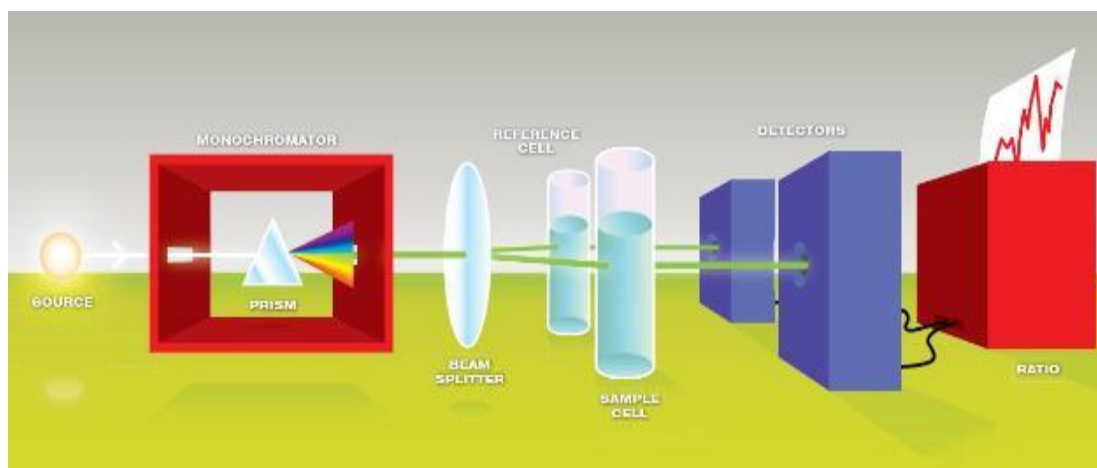


Figure 4: Basic structure of a UV/VIS spectrometer

After the light source, as shown in Figure 4, there is a monochromator. This device focuses the light source on a diffraction grating which decomposes the incoming light into

its component colours of different wavelengths, but more efficiently than a prism. The beam splitter is typically used in two-beam spectrometers where the light is transported one time to the sample cell and one time to the reference cell. The detector afterwards, which is a photocell, is converting the electromagnetic radiation into an electric signal. Then a spectrum can be printed and saved.

Spectroscopic methods for quantitative analysis

The system of using photometers to analyse chemical parameters is not new. It was invented at the beginning of the 20th-century as Pulfrich - Photometer at Zeiss in Jena (Perkampus, 1992).

When measuring with spectrometry, the substance-specific attenuation of electromagnetic radiation due to absorption is used (Hubert Hain, 1994). The interaction of the electromagnetic waves with the molecules is the basis for the application of this measuring principle. The shape of a spectrum shows the absorption of the media in which the spectrometer is held. This difference between emitted and continuous energy is plotted against the wavelength or wavelength ranges. The resulting excitation of the molecules due to energy absorption can be distinguished excitation of the electrons in the UV and VIS spectral range.

It is based on the theory of Bohr-Einstein's frequency relationship, which leads to the measurement of absorption and emissions of material like Metals, Anions, Cations, organic compounds:

$$\Delta E = E_2 - E_1 = h * \nu \quad \text{Equation 2}$$

This equation links the atomic or molecule energy states E_i with the frequency ν of electromagnetic radiation. In spectroscopy, the frequency ν is often changed with the wavenumber $\tilde{\nu}$ while:

$$\nu = \frac{c}{\lambda} = c * \tilde{\nu} \quad \text{Equation 3}$$

So Equation 3 can be transferred in:

$$\Delta E = E_2 - E_1 = h * c * \tilde{\nu} \quad \text{Equation 4}$$

Absorbed or emitted wavelength or frequency can now be assigned to energy differences or also to a specific energy-level difference:

$$\text{Equation 5}$$

$$\tilde{\nu} = \frac{\Delta E}{h * c} = \frac{E_2}{h * c} - \frac{E_1}{h * c} = T_2 - T_1$$

T_i is the term value which is corresponding to the energy level. Nevertheless, energy levels that lead to molecular excitation are described by Plank's equation, which corresponds to a derivative of Equation 5:

$$E_2 - E_1 = \Delta E = \frac{h * c}{\lambda} \quad \text{Equation 6}$$

In the quantitative or qualitative measurement, the specific attenuation of the electromagnetic radiation is applied by the absorption. In comparison, the emission measurement is based on the principle of electromagnetic radiation intensity, which is generated by high temperature on a sample. These measurement principles are shown again in the following illustration (Hubert Hain, 1994):

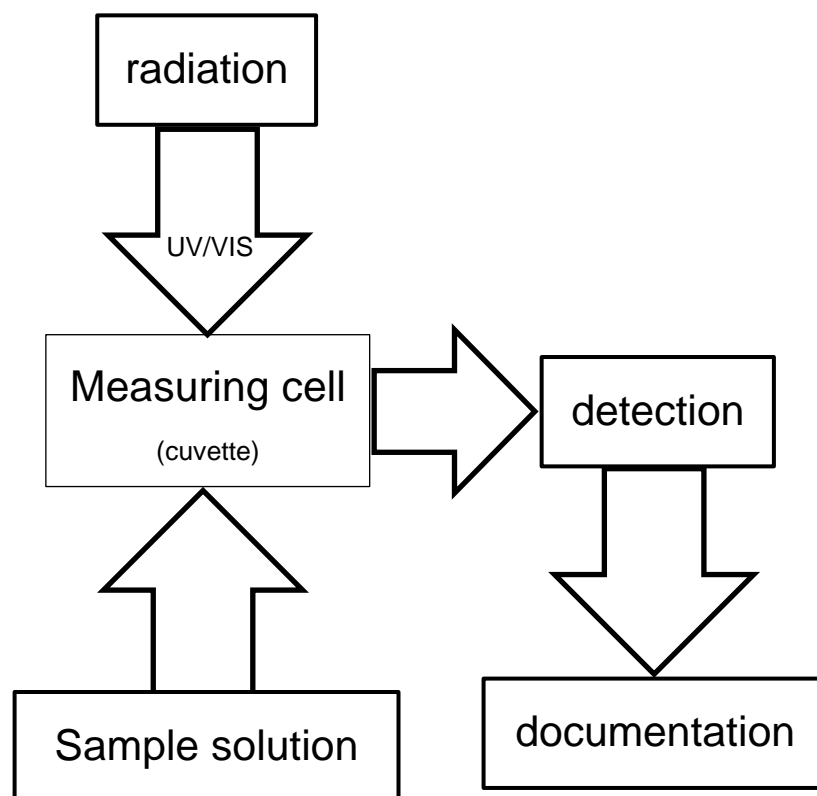


Figure 5: Principle of spectrometry (UV/VIS)

Bouguer-Lambert-Beer Law

This law forms the mathematical and physical basis of light-absorption measurements, like in Infrared or Ultraviolet/Visible measurement (Perkampus, 1992). The absorption is proportional to the concentration of a sample. This makes it possible to convert a spectrum with a calibration line in a concentration (Royal Society of Chemistry, 2009).

$$A = \log_{10} \left(\frac{I_o}{I} \right) = \varepsilon * c * l \quad \text{Equation 7}$$

A = absorbance

I_o = Intensity of the light

I = Intensity of the light in the detectors

l = optical path length, i.e. cuvette length (cm)

c = concentration of the solution

ε = constant of the molar extinction

The absorption of several samples with a measured concentration, are plotted against their corresponding concentrations. This produced absorbance versus concentration leads to a linear graph when the law of Bouguer-Lambert-Beer is obeyed. The graph is also known as the calibration graph.

With a calibration graph, it is possible to determine an unknown concentration of a sample by measuring the absorbance.

- The different analysis methods are also applied to various environmental parameters as Anions, Cations, Colour, Organic compounds (Hubert Hain, 1994)

At the end of a UV/VIS measurement is always a spectrum, which is the basis to get the desired parameter value (BOD₅, nitrate, turbidity, etc.). But so that a measurement value can be generated from a spectrum, the principle of chemometric must be applied.

Chemometrics

The discipline chemometrics is developed because of the connection between computers and chemistry such as the correlation of concentrations (Langergraber, et al., 2004). As it started in the early seventies, some analytical groups worked with statistical and mathematical methods which are now known as chemometric methods (Otto, 1999). The actual definition for the word chemometrics is:

- design or select measurement methods and experiments which mathematical relationships follow
- To provide maximum chemical information by analysing chemical data

With this method, analytical devices can measure the data and can convert them into readable concentrations (Andris, et al., 2018). Like a spectrometer where the output is only a spectrum, and the chemometrics is calculation a concentration. There are two methods normally used for UV/VIS spectrometer, the PLS (partial least squares) and the MLR (multiple linear regression) who is usually applied (Calibration of a UV/Vis Sensor for Sulphide Monitoring in Sewer Systems, 2017; Torres, et al., 2008). In this work, only the multiple linear regression is applied which described below.

Multiple linear regression

In this multivariate modelling, several independent and dependent variables may operate. It consists of two or more unknown variables and is an extension of the linear regression (Otto, 1999). The formula for the multiple linear regression is:

$$y_i = \beta_0 + \beta_1 * x_{i1} + \beta_2 * x_{i2} + \dots + \beta_p * x_{ip} + \epsilon \quad \text{Equation 8}$$

y_i = dependent variable

x_{i1} = explanatory variables

β_0 = y-intercept (constant term)

β_p = slope coefficients for each explanatory variable

ϵ = error term (also known as the residuals)

The application of this regression can be explained by photometric analysis.

In the beginning, the program receives a so-called absorption spectrum, which follows the law according to Bouguer-Lambert-Beer. Subsequently, the analytical measurements are added and assigned to the spectra. Now the dependent and the explanatory variables

are set, and the equation can be started. The result is a calibration line where the absorptions are assigned to concentrations.

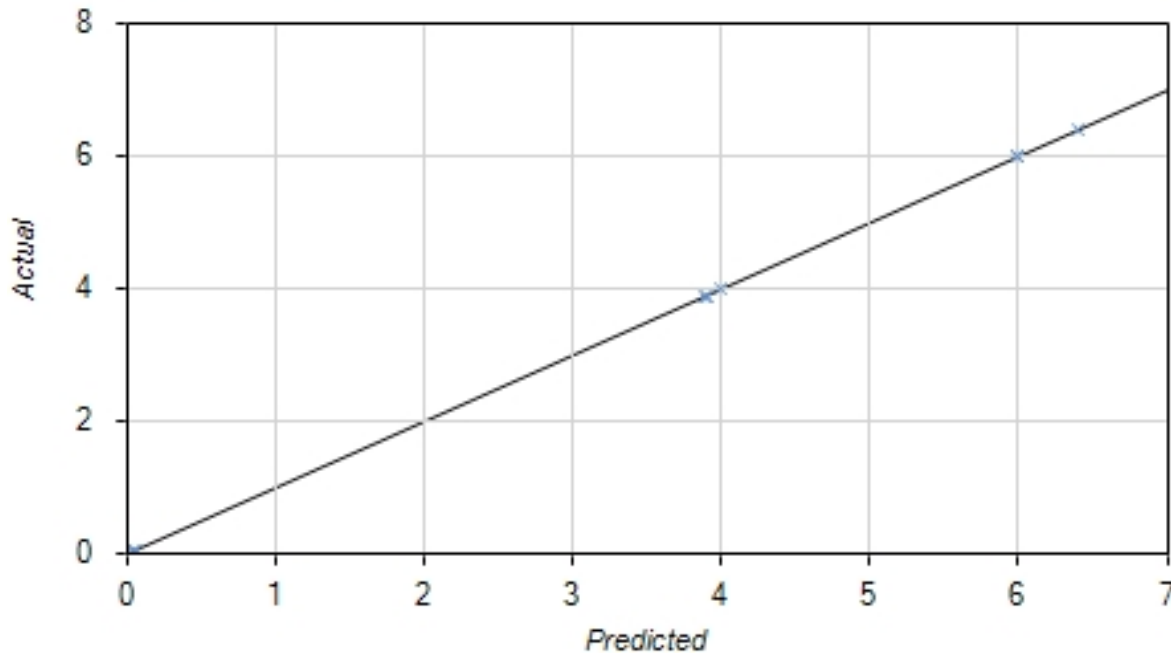


Figure 6: calibration line after the multiple linear regression

Outliers

Low prediction errors do not influence the models.

Nevertheless, samples which do not follow the same model as the rest of the data are called outliers. When a calibration line has too many outliers, the line could be wrongly interpreted, and the results of the concentration could be wrong. As a good example, it is good to ask the manufacturer, which is the limit of the outliers for a good result.

3.5 On-line UV/VIS spectrometers

Several manufacturers in the market produce UV/VIS spectrometers. The differences of them are often the detectable parameters as well as the light source or the construction.

S::can Messtechnik GmbH

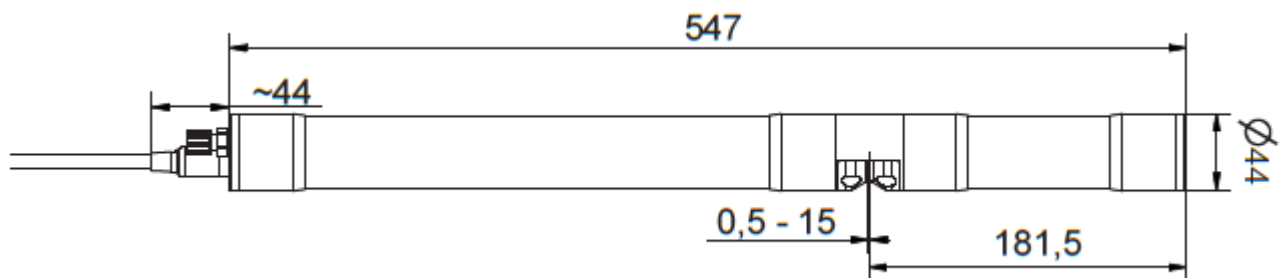


Figure 7: Spectro::lyser (S::can)

Submersible Probe which can be attached to all objects in water to measure in-situ and also in flow fitting (measuring station) (S::can, 2019). 5 inserts with different fixed path length (0.5, 1, 2, 5, 15). Cleaning of the light path with pressurized air.

Light source: XENON Lamp

Parameters (S::can, 2019):

- *Biological oxygen demand (BOD₅)*
- *Chemical oxygen demand (COD)*
- *Acoustic Force Spectroscopy for single-molecule measurements (AFS)*
- *Turbidity*
- *Nitrate nitrogen (NO₃-N)*
- *Total organic carbon (TOC)*
- *Dissolved organic carbon (DOC)*
- *Organic constituents (UV 254)*
- *Colour*
- *benzene, toluene, ethyl benzene and xylene (BTX)*
- *Ozone (O₃)*
- *Assimilable organic carbon (AOC)*
- *Fingerprints, spectral-alerts, Temperature and Pressure*

REALTECH Inc.

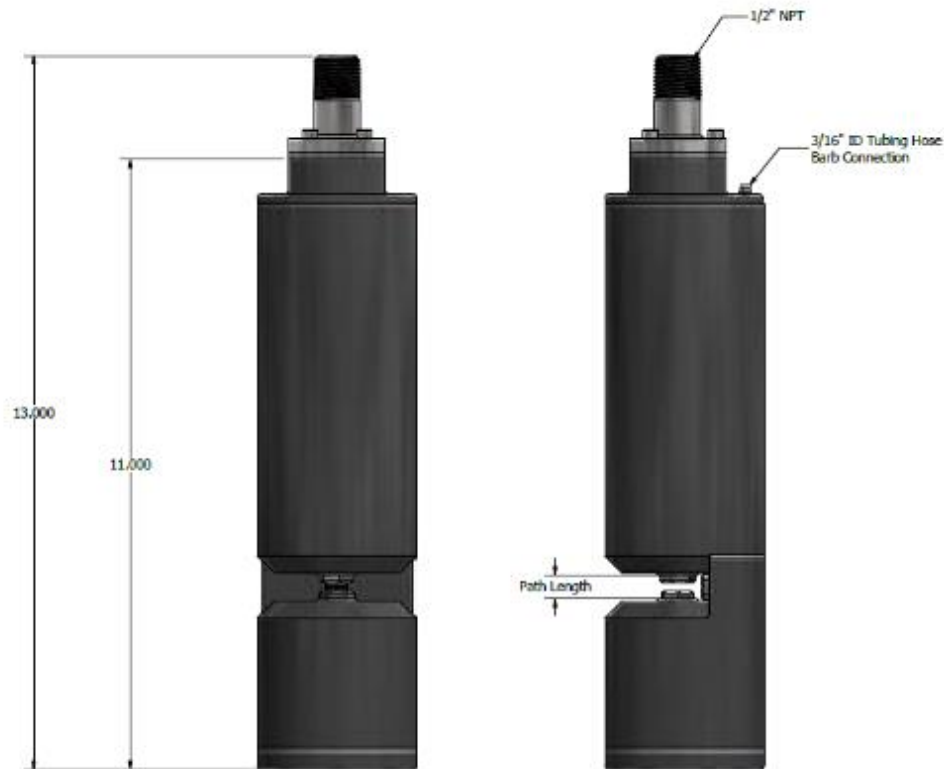


Figure 8: Multi-Wave Probe (REALTECH Inc.)

Submersible Probe which can be installed directly in in-situ using a mounting kit or attached to a tank wall or railing (REALTECH Inc., 2019). 4 Models with different path length (1, 2, 4, 10mm). Cleaning of the light path with pressurized air.

Light source: LED

Parameters (REALTECH Inc., 2019):

- *Biological oxygen demand (BOD₅)*
- *Chemical oxygen demand (COD)*
- *Total organic carbon (TOC)*
- *Dissolved organic carbon (DOC)*
- *Organic constituents (UV 254)*
- *UV Transmittance (UVT)*
- *Total suspended solids (TSS)*
- *Colour*
- *Ozone (O₃)*

WTW Laboratory & Field Instruments

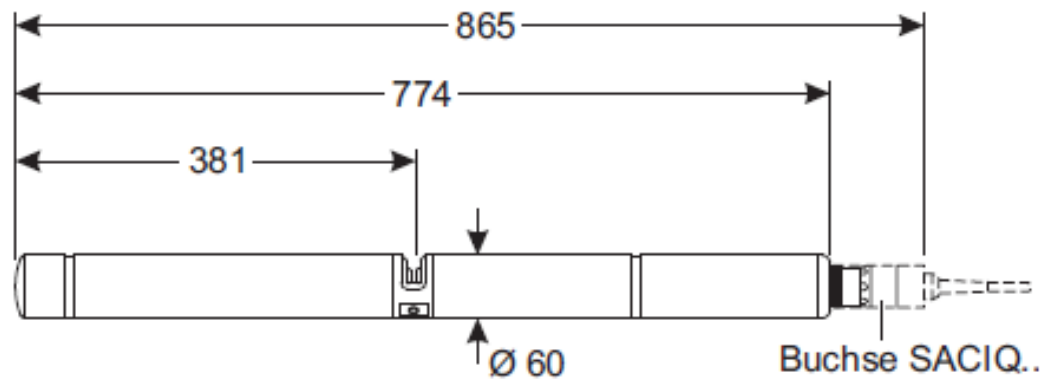


Figure 9: NiCaVis® 705 IQ (WTW Laboratory & Field Instruments)

The optical measuring method of these sensors enables the continuous measurement of the parameters carbon and nitrogen directly in the medium (WTW Laboratory & Field Instruments, 2019). In this method, the information of the entire spectrum is evaluated, whereby several parameters can be determined simultaneously. At the same time, cross sensitivities of individual parameters and disturbances such as turbidity are eliminated. Equipped with maintenance-free WTW ultrasonic cleaning. There are two models with a different path length of 1 and 5 mm and they can be placed directly in the water (in-situ).

Light source: XENON Lamp

Parameters (WTW Laboratory & Field Instruments, 2019):

- Biological oxygen demand (BOD₅)
- Chemical oxygen demand (COD)
- Nitrate nitrogen (NO₃-N)
- Nitrite nitrogen (NO₂-N)
- Total organic carbon (TOC)
- Dissolved organic carbon (DOC)
- Organic constituents (UV 254)
- UV Transmittance (UVT)
- Total suspended solids (TSS)

Go-Systemelektronik GmbH



Figure 10: BlueScan (Go-Systemelektronik GmbH)

The BlueScan UV/Vis spectrometer system enables the simultaneous acquisition of multiple parameters and offers a variety of control functions (Go-Systemelektronik GmbH, 2019). The use of chemometric methods allows the accurate collection and analysis of a variety of properties of water, suspended solids and dissolved constituents. For the evaluation, the system uses the entire UV to the near-infrared (200-720 nm) absorption spectrum. The spectrometer system has an adjustable optical path length (1-30 mm), which allows optimal adaptation to the respective application. This makes it possible to obtain accurate measurements of the water used for the drinking water. Cleaning of the light path with pressurized air.

Light source: XENON Lamp

Parameters

- *Biological oxygen demand (BOD₅)*
- *Chemical oxygen demand (COD)*
- *Nitrate nitrogen (NO₃-N)*
- *Ammonium nitrogen (NO₄-N)*
- *Total organic carbon (TOC)*
- *Organic constituents (UV 254)*
- *Total suspended solids (TSS)*
- *Phosphate phosphorus (PO₄-P)*
- *Turbidity*

In a process in 2017, all spectrometers were compared and as the probe of Go-Systemelektronik is the only device which can provide a measurement for ammonia and phosphorus in one spectrometer it was selected (Allabashi, 2017).

To reach the need for good quality measurement it is inevitable to measure the reliability of the devices who gain the data. This measurement of the measurement is called validation and is very important for companies and customers to know how good the device or system is working.

3.6 Calibration and Validation

The calibration of the measurements is one of the basic conditions to be able to carry out a validation. The calibrations include:

- global calibrations
- local calibration.

The global calibration is a calibration which is normally pre-installed on each measurement device. This calibration is usually stated with a high precision in the measurement (Langergraber, et al., 2004).

Due to special water characteristics the sensor must be calibrated additionally at the measurement location (local calibration). This local calibration is improving the trueness, precision and long term stability of the measurement results (Rieger, et al., 2004).

Validation of the method is a key activity of chemical analysis, which is essential for reliable results. The more complex the method, the more important and extensive the validation. This information is relevant to both, the laboratory (to be able to rely on the results or to change the method accordingly if performance does not meet expectations) and to the customer (University of Tartu, 2019). In addition to the actual need for validation, there are increasing regulations for laboratories regarding to the validation procedure.

The importance of validation has led to the creation of a variety of laboratory validation guidelines that are both universal and industry specific. Although there is general agreement about the different validation parameters to be evaluated, there are differences in the details and methods used for the validation and acceptance criteria.

Different recommendations and different terminologies can be found in different guidelines. In this work, the international standard ISO 15839:2003(E) is used (International Standard, 2003) for the validation process.

The validation in this work is used to determine the power of the In-Situ System for customers after a new development of a product that they can rely on when they make their purchase. These customers can be companies, public institutions, or others. It is also very important that the work is done properly so that others do not have to work with incorrect information. It is therefore good to show that your product is suitable for the purpose. There are three important aspects of validation (University of Tartu, 2019):

- **Experimental**
Experiments should always be carried out to correctly validate the method. Theoretical considerations are not enough, but theoretical knowledge can be very helpful when planning the validation process. In this work, indoor and outdoor tests are carried out with different scenarios in order to get a good experimental overview
- **Objective**
The results during the validation should also be accompanied by suitable statistical tests that provide an objective overview of the results. So that not only the results are analysed based on someone's subjective opinion.
- **Scope related**
The results are also related to the scope of the method. For example, it is not possible to use the validation for other equipment's.

4. Material and methods

4.1 Autonomous robotic boat

The basis for the work was a model boat equipped with sensors. Development and production were realised with project partners throughout Europe. One crucial point is the data processing, as the measurements are directly sent from the BlueBox, which is a small computer on the boat, to the BlueGate. The BlueGate on the other side of the data exchange is a server, where the data from all BlueBoxes are stored. *Figure 11* is showing the built-in electronics, in the top compartment of the autonomous boat, where the following parts can be found:

- the taken apart BlueBox of the company Go-Systemtechnik
- Platypus Printed Circuit Board (PCB)
- Processor PCB
- WLAN-repeater
- GPS-receiver
- Mobile phone antenna (BlueGate connection)

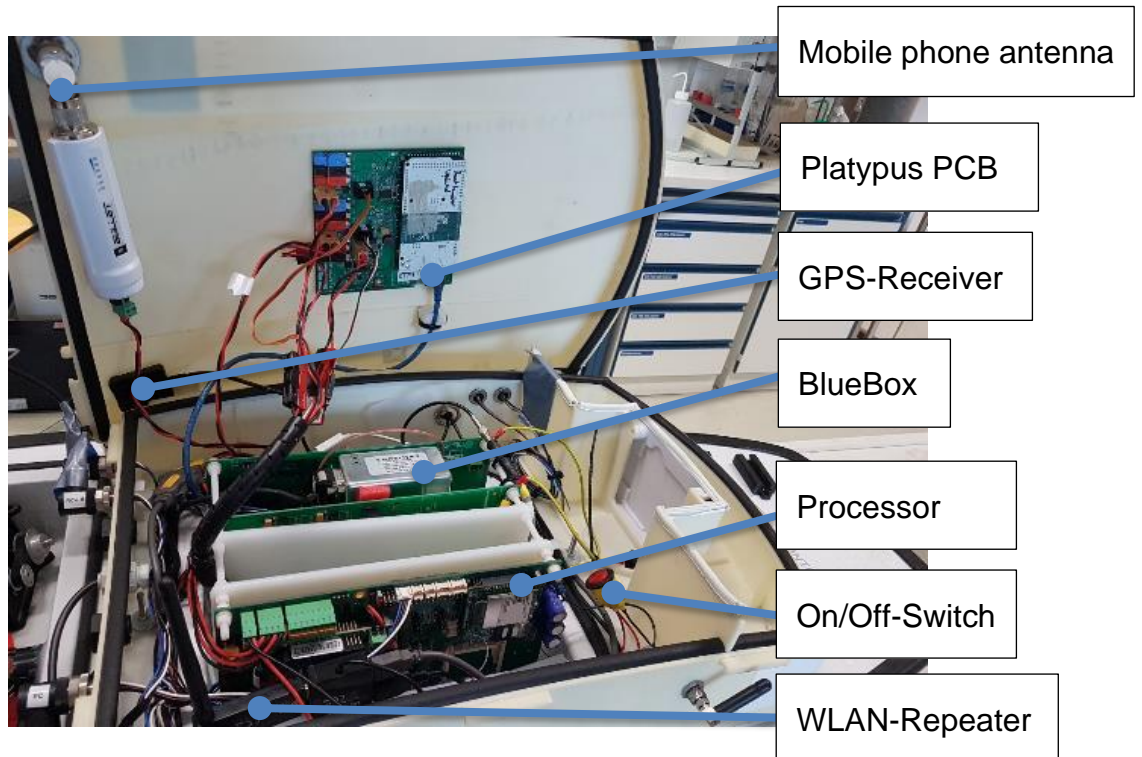


Figure 11: Open top of the boat

The boat is watertight sealed, using caps for the main compartment and rotating closures for the engine compartment. At the back is the engine compartment, in which the two engines and the battery can be found. The engines are water-cooled to avoid their overheating during operation. On the left side of the boat in *Figure 12* is the outlet for the fibre optic cable, which ensures the connection between BlueBox and UV/VIS spectrometer.

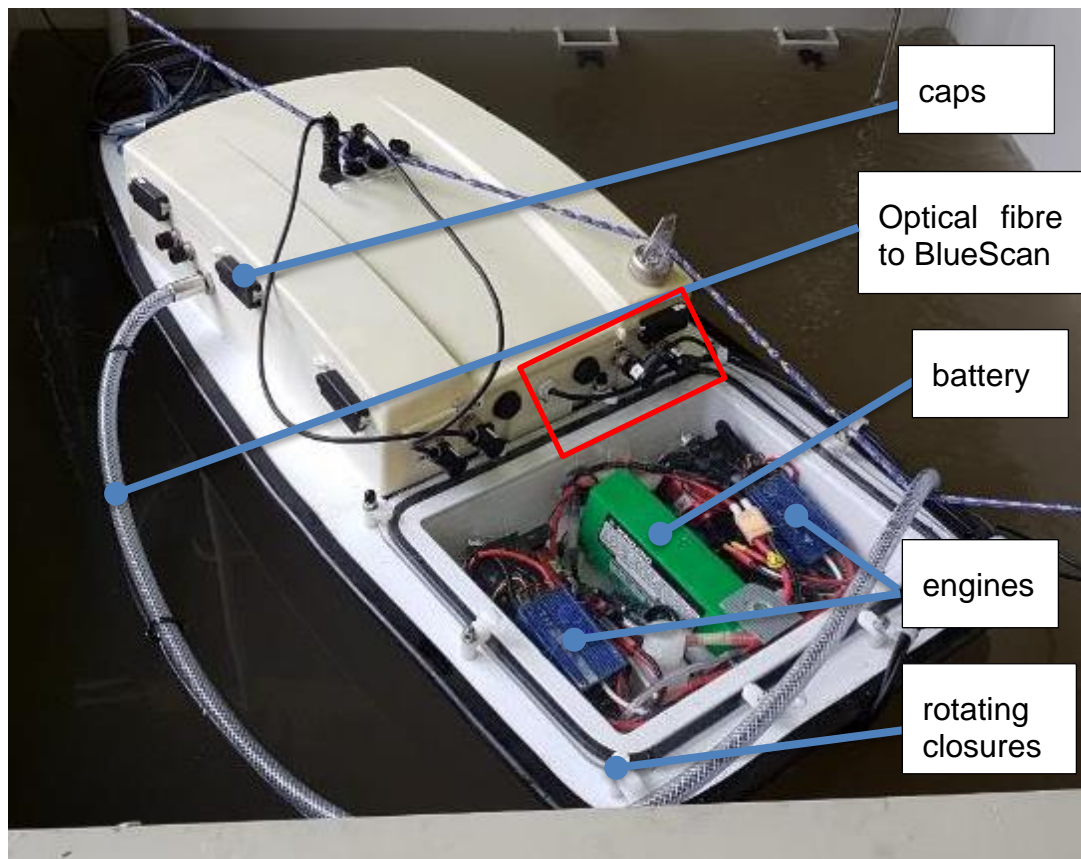


Figure 12: Closed top of the boat

In the red-marked area are the outlets for the remaining sensors (Dissolved Oxygen, pH, Electrical Conductivity). These sensors are also attached at the bottom of the boat next to the UV/VIS spectrometer.

Measurement devices

All sensors must be tightly fixed to the bottom part of the boat that a long-term recording can be established. For this reason, the probes are mounted with slings on a plastic platform which can be attached to the boat as seen in Figure 13.

- EC-probe (inductive)
- UV-VIS-Spectrometer
- pH-probe
- DO-probe (amperometric)

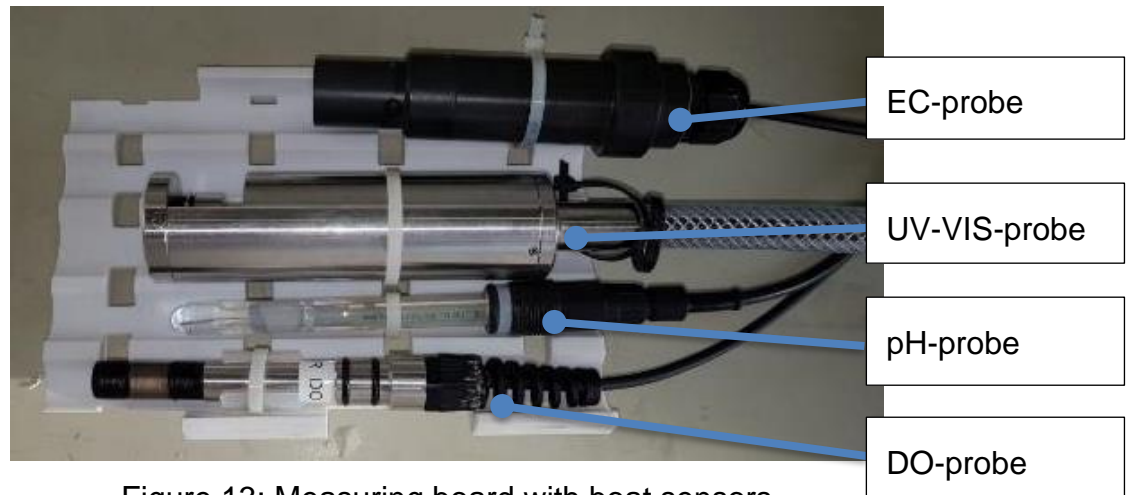


Figure 13: Measuring board with boat sensors

On the other side of the board, sensors for the reference measurements are attached.

The measurement devices are shown in Figure 14.

- EC-probe (conductive)
- pH-probe
- DO-probe (optical)

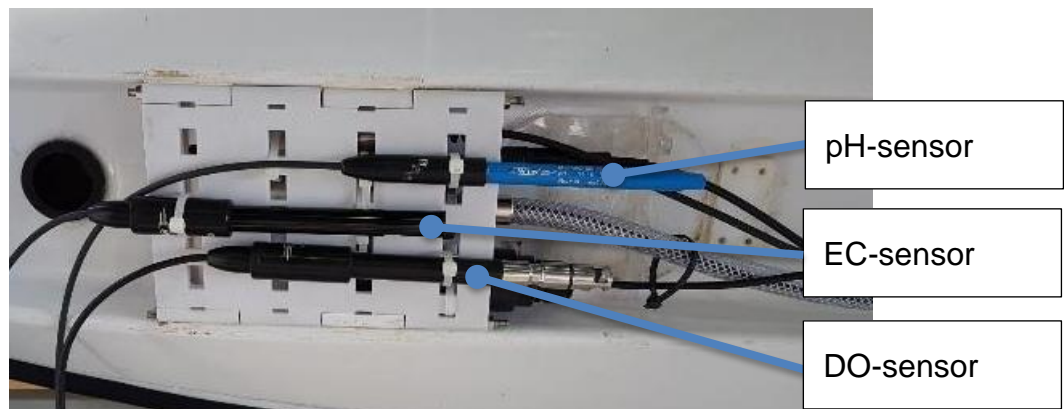


Figure 14: Measuring board with boat sensors and WTW sensors

4.2 Indoor Validation

4.2.1 General description

The main purpose of the validation of the above described equipment is the evaluation of its performance, regarding to detection of municipal wastewater pollution in a surface water body (river). This is achieved by following the rules of the validation process as described in the following paragraphs.

Requirements for the trial

- The test facilities shall match the requirements by the manufacturer or supplier
- The facilities should be able to record data
- It shall be possible to change the calibration of the measurement within less than 10% of the response time declared by the manufacturer or supplier
- The testing facilities should include laboratory devices to compare the values

The analysing equipment may automatically indicate any malfunctions by its diagnostic system. For monitoring purpose, the plot of the measurement on a response chart is necessary (International Standard, 2003).

Test procedures

The following performance characteristics of the system are included in the validation procedure:

Limit of detection (LOD)

It is the lowest value which is significantly greater than zero used for a determinant that can be detected. This value is three times the standard deviation of the measurements with a concentration of 5% (Kromidas, 1999).

Limit of quantification (LOQ)

This is the lowest value of a determinant which can be measured with an acceptable level of accuracy and precision. It is ten times the standard deviation of the measurements with a concentration of 5% (Kromidas, 1999).

Repeatability

Repeatability is the precision of measurement under repeatable conditions. It is determined for both “high” and “low” values (20% and 80%) and calculated as the standard deviation (Kromidas, 1999).

Lowest detectable change (LDC)

LDC is the smallest significantly measurable difference between two measurements, is also determined for “low” and “high” values (20% and 80%) and then calculated like the limit of detection (International Standard, 2003).

Accuracy

It is the closeness of a measured value with the accepted reference value. It is calculated as a %-value which describes the precision of the measurement (International Standard, 2003)

The indoor validation process, according to Annex A, ISO 15839:2003 is used to determine the performance characteristics of the measuring system. The tests were carried out with Danube water, whereby a calibration of the autonomous boat was necessary at the beginning.

Procedure

The process of validation will take several weeks, where a strict timeline needs to be followed to deliver results. The following steps describe an indoor measurement trial, including calibration of measuring equipment's and validation of the system:

- Preparation of the measurement
- Taking water samples from the Danube River
- Measurement procedure
- Evaluation process

These four steps are described in more detail in the following chapters.

4.2.2 Preparation of the measurement

At the beginning of each measurement, the instruments for measuring of pH, dissolved oxygen and electric conductivity had to be recalibrated or checked.

pH:

Reference Probe

The calibration of the pH probe is based on the measurement of a buffer solution with a pH of 4 and 7. At pH 7, which represents the neutral state, the meter should output a voltage of 0V. If the pH drops, the voltage becomes negative if it increases, the voltage becomes positive. For pH 4, the voltage should be -180mV. At the end of the process, a slope for the calibration of about -58.9 mV / pH should be displayed on the device.

Boat probe

The calibration is carried out with the same steps. Very important is the temperature of the two measured buffers, as they have to be considered in the calibration process.

Electrical Conductivity

Reference and Boat probe

Calibration is not necessary, but a check is made to ensure the correctness of the measurement. To do this, the sensor is immersed in clean water for the first measurement, a result of around 0 μ S is displayed. Subsequently, drinking water (~ 330 μ S) and a control sample (~ 720 μ S) are measured.

Dissolved Oxygen (DO)

Reference probe

For the measurement of DO, the probe also does not need a calibration but is tested of its performance. To obtain this is immersed into tap water to measure a value of tap water around 9 mg/l O₂.

Boat probe

Because the measurement principle is different the check of the sensor is also a little bit different. In the beginning the sensor is placed into the air with no surface contact that a calibration of the sensor could be made. After that it is also checked of its performance in tap water however it should be noted that the sensor must be moved for the measurement to work properly.

BlueScan (spectrometer)

Between all measurements, the spectrometer needs to be in clean water that the glass openings for the light beam do not get dull. Before the first measurement, the sensor is

immersed in a beaker glass of citric acid ($C_6H_8O_7$) for about five minutes. After this process, the two glass openings are cleaned with a detergent and a cotton swab.

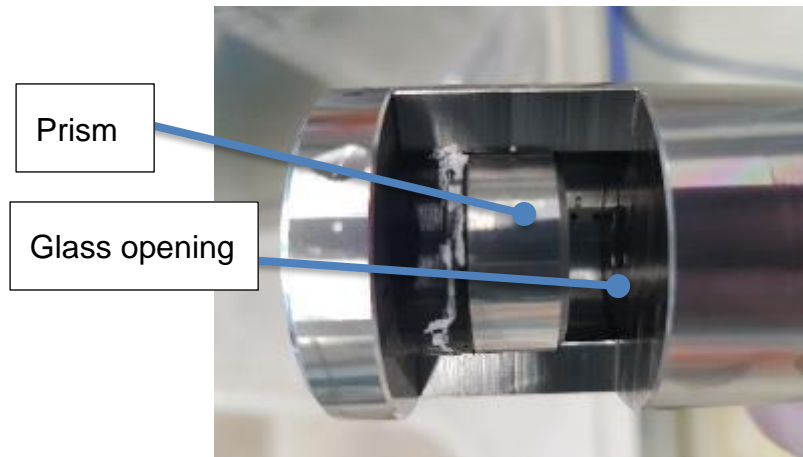


Figure 15: BlueScan Measuring Head with prism

Subsequently, the first measurement in clean water is carried out. An example is shown in Figure 16.

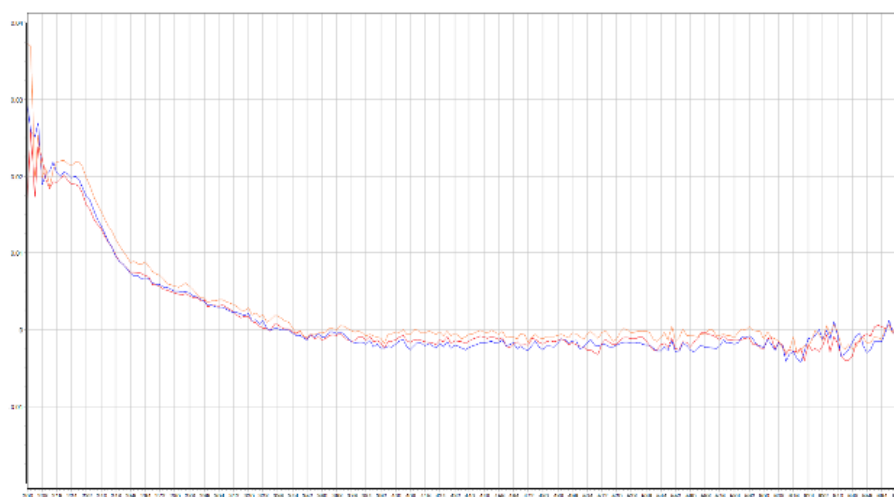


Figure 16: Graph of the Absorption Spectrum

In the event that the absorption of clean water during a first measurement is less than 0.03, as can be seen in the figure above, there is no need to recalibrate. If this is not the case, the recalibration must be carried out. This is a process that is carried out by the software itself and requires no additional effort

On the other hand, it is of high importance to make an intensity adaption in clean water. It is required in order to use the measuring range in the application environment so that the digital absorption values are in the linear range from 0 to 32000. The absorption value depends on the intensity (light intensity) i.e. the number of flashing lights per

single measurement. Calibrating the intensity in clean water is part of the intensity setting (Go-Systemelektronik GmbH, 2019). This intensity calibration adjusts the intensity so that the maximum value of raw spectra (MVR) is in the range of 2600-30000. In Figure 17, the outcome of this calibration is represented by the graph, which indicates an intensity of around 28,500 units in this case.

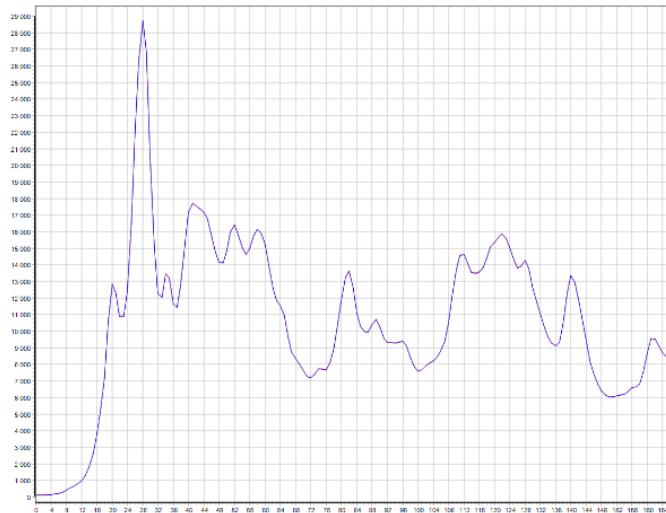


Figure 17: Graph of the Intensity Spectrum

Technical problems with the spectrometer were identified in the first two weeks. These problems were recognizable by incorrect measurements due to water inclusion in the prism. As a result, the prism was replaced, and the measurement continued.

Sample bottles

For the test, eighteen sample bottles are needed, nine bottles are for the measurements of phosphorus, Biological oxygen demand and nitrate for tree measurements. The other bottles are additionally acidified with H_2SO_4 (1 mL of H_2SO_4 (1:2) in 1L sample). This acidification is carried out that microbial degradation is minimized as this would reduce the measured concentration (Ramesh Kumar, 2015). The amount of water sample is calculated for three measurements each spiking level described later in chapter 4.2.4.

Boat

Before attempting, the functions of the boat must be checked and tested. This includes checking the connection between the boat and all sensors as well as the correctness of the imported calibrations for the spectroscopic measurements.

4.2.3 Taking water samples from the Danube River

For the measurement on the test facility, an amount of about 600l Danube water has to be taken from the Danube channel. To achieve this purpose following utensils are needed:

- Water tanks (altogether ~ 600l)
- Pump
- Generator (with a filled tank with gasoline)
- Cable drum
- Water pipe

The suction point was located opposite the Holzgasse in the 19th district, as shown in Figure 18.

The generator is then positioned and started. It must be ensured that no consumer (pump) is connected; otherwise, the danger of an overvoltage arises. This process can be seen in Figure 19



Figure 18: Water suction point at the beginning of the Danube channel (Basemap Vienna)



Figure 19: Electrical pump and water pipe in the water

Back at the test facility, the measurement tank is filled. If that the water level in the tank reaches 550l. This is shown in Figure 20.

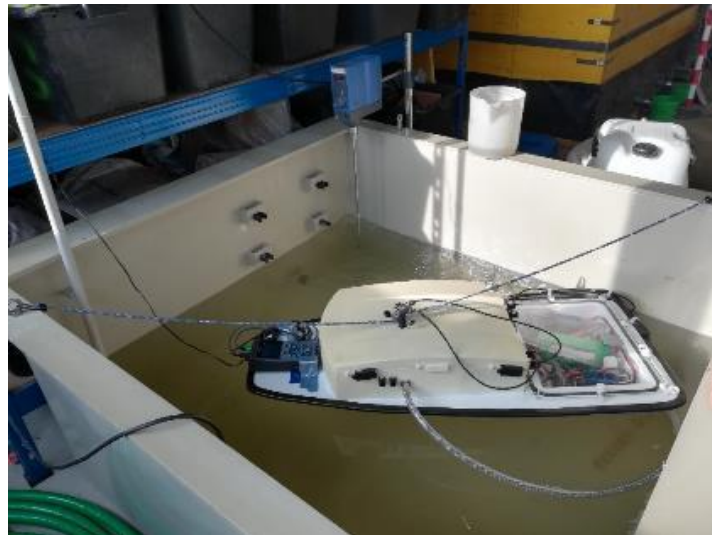


Figure 20: Experimental site for indoor validation

4.2.4 Measurement procedure

Before starting the measurement process, the working order needs to be described. This starts with the calculation of the amount of wastewater needed for the experiment, which

is based on the TOC content of the influent and effluent of the Sequence Batch Reactor, as described in Table 2.

Table 2: Measurements of the Influent and Effluent of the SBR

	TOC [mg(l)]
Influent	240
Effluent	0

The amount of wastewater for the tank can be calculated as shown in the following example:

$$1:2 \Rightarrow 240 \frac{\text{mg}}{\text{l}} + 0 \frac{\text{mg}}{\text{l}} = 240 \frac{\text{mg}}{2\text{l}} = 120 \frac{\text{mg}}{\text{l}} \Rightarrow 1:15 = 8 \frac{\text{mg}}{\text{l}} \text{ TOC}$$

$$\text{Volume of the tank} = 550\text{l} \Rightarrow \frac{550\text{l}}{15} \sim 40\text{l}$$

Thus, an amount of 40 l of influent and effluent is necessary to expect a TOC change of about 8 mg / l. For the measurement, a three-step spike with a duration of two hours per each stage for the validation is set. In the first step, a measurement in Danube water without additional pollution is carried out. In the second, the first load of wastewater is added. The last step wastewater is added again, and then after two hours, the series ends, as can be seen in Figure 21.

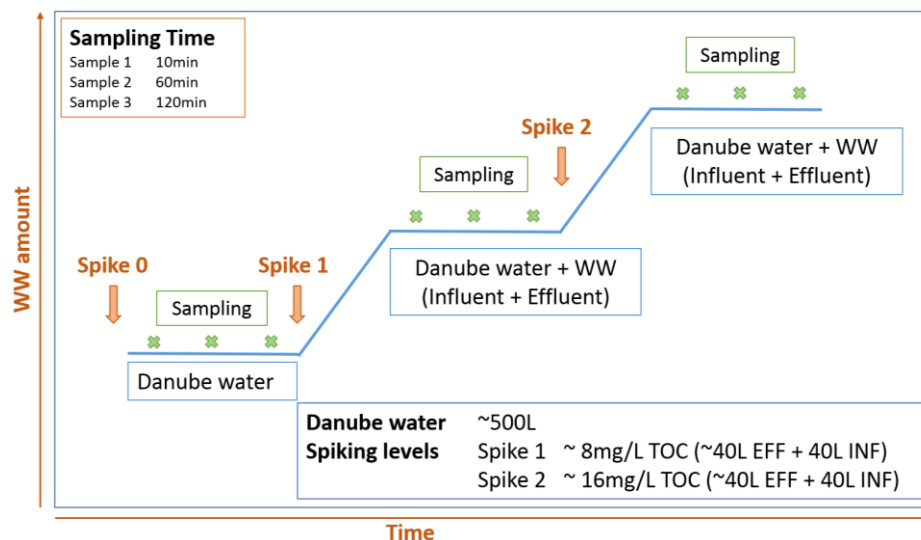


Figure 21: Measurement procedure with all spikes and sampling points

At every measurement step three samples for the reference measurement, are taken at 10, 60 and 120 minutes after the spiking so that a possible measurement error can be recognized (Schmusch, 2005).

It is important to ensure the correct amount and contamination-free filling of the tank with Influent and Effluent.

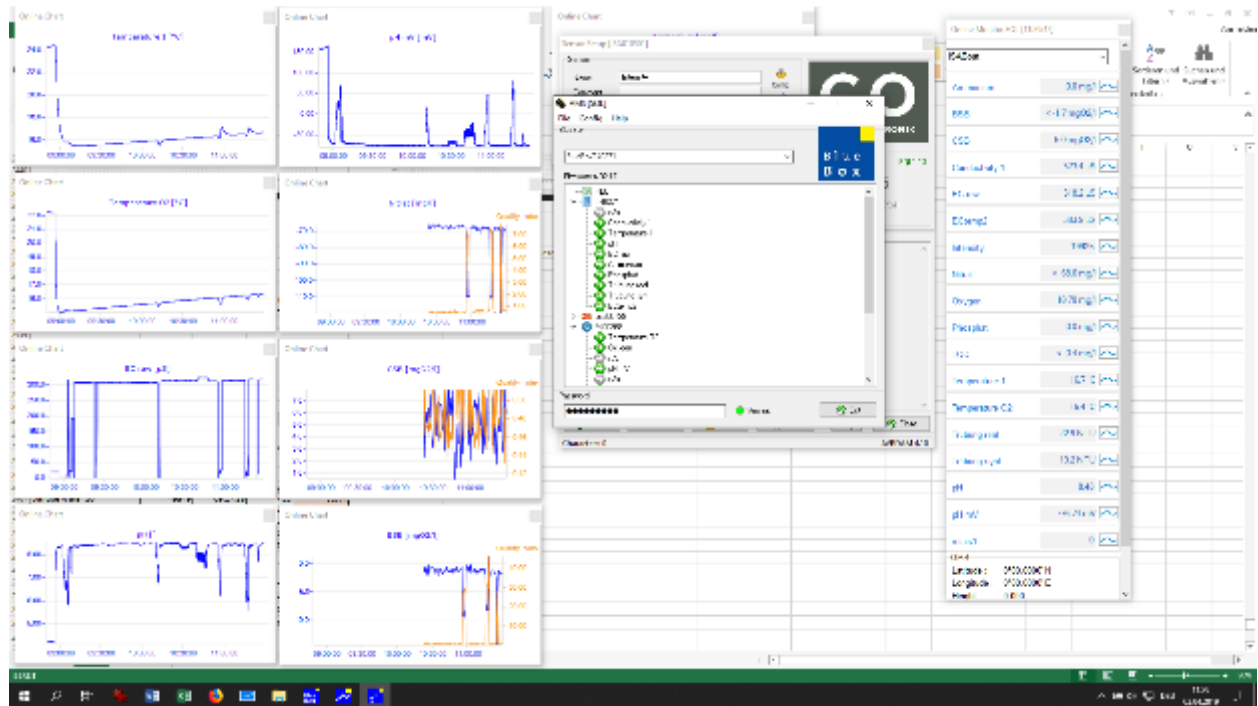


Figure 22: Measurement Computer with live graphs

During the experiment, all probes continuously record data at pH, DO, EC every 5 seconds and at the UV/VIS probe every 30 seconds. In *Figure 22*, the desktop picture of the measurement computer is displayed where all graphs of the different probes are displayed. With this function, it is possible to follow if the measuring and recording process was working properly.

4.2.5 Evaluation process

After every measurement process, the data from the reference device and the blue box were copied and stored on the measurement computer. To produce readable graphs and tables with a large amount of data, some things have to be considered. In the beginning, the times for the beginning of the measurement must be equated.

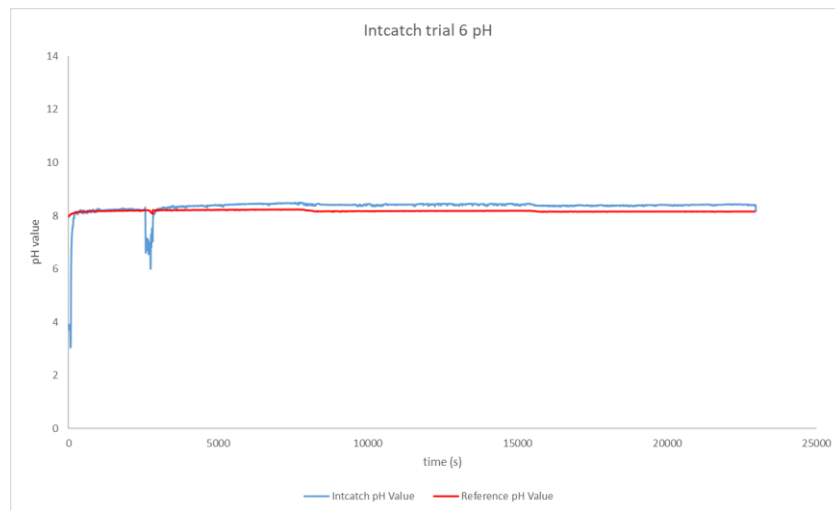


Figure 23: pH Measurement graph after the data evaluation

This process is critical so that the measurements for the pH, EC and DO sensors from the boat and the reference measurement coincide in time, as shown in Figure 23 for pH. In red colour, is shown the reference measurement and in blue the sensor from the boat.

In comparison to the measurements with these probes, the UV/-VIS spectroscopy are displayed with the measurements from the laboratory who are shown as points. This process normally takes a little bit longer, because of the longer time to make the reference analysis.

Figure 24 shows the graph of a phosphate measurement; the difference between the colours brown and purple is due to the calibration used. The brown line shows concentrations calculated from a calibration based on all measurements performed in the laboratory, while for the purple line a calibration of the initial phase has been used. This evaluation had to be carried out in further consequence for all measured values.

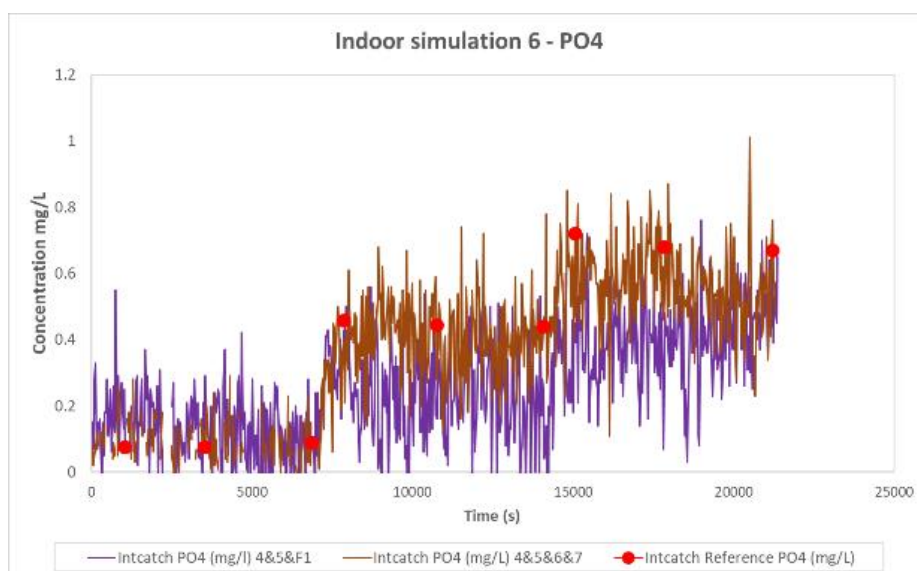


Figure 24: PO4 Measurement graph after the data evaluation

A calculation of the mean values and standard deviations of the individual stages for the validation was then carried out with all results.

4.3 Outdoor validation

4.3.1 Requirements for the trial

Field tests supplement laboratory tests and include the entire measuring chain, consisting of the online sensor and all necessary sampling, pumping and conditioning devices. The aim of field tests is to determine the long-term ability of a measuring chain to carry out reliable measurements. Field trials are location-specific with regard to the dynamic range of the sample and the type of water and event-dependent with regard to the ambient conditions. Therefore, the operating conditions specified by the manufacturer / supplier must be observed during the entire test and the determined performance characteristics must always be stated in connection with information on the test location and the actual operating conditions during the test (International Standard, 2003).

4.3.2 Test procedures

The test procedures are very similar to the indoor trials shown in chapter 4.2.1.

The main goal of the out-door validation is to assess the performance of the integrated system under real conditions and to deliver complementary information to that of in-door validation. These include firstly the features relevant for the working of the system and secondly the influence of the electrical and mechanical components on the accuracy of water quality measurement. During the validation work, it turned out that the grounding has a strong influence on the signal of the EC, pH and DO probes.

The performance characteristics of water quality under outdoor conditions are not carried out as in indoor validation since the calibration does not include enough reference measurements for an outdoor calibration.

4.3.3 Preparation of the outdoor validation

The out-door validation took place at the New Danube, as can be seen in Figure 25.



Figure 25: New Danube at Freudenu (source: Google Maps).

In the out-door trial, the boat system is also tested while using the GPS-Antenna, the remote control or the self-driving and manoeuvring system. These functions cannot be checked in-door because the GPS antenna is not working inside a building.

4.3.4 Validation procedure

The main focus of this part of validation is the assessment of system features, relevant for the working process of the integrated system, as following:

- Signal sender and receiver
 - Global Positioning System (GPS)
 - Remote control antenna (RC)
 - Mobile network
- The autonomous control unit (Tablet)
 - Base map included
 - Control graphical user interface (GUI) installed
- The connection between boat and autonomous control unit (Mobile phone)
 - Compass
 - Boat server installed
- Movement controller as a backup function
- Data mapping
 - Measurements with GeoReference

- Working with WAQUIN as a platform to display the results of the measurement
- Working with WAIS for the interaction with the data server BlueGate

Additionally, the validation of the analytical performance of the system under out-door condition is carried out in this phase.

4.3.5 Evaluation process

The capability of the sender and receiver is tested during the first step of the validation process. This includes the correct detection of the position as well as the transmission of the data to the tablet. When this process is complete, the integrated system is placed in the water. Then a route is created on the tablet, which is to sail the boat shown in Figure 26.

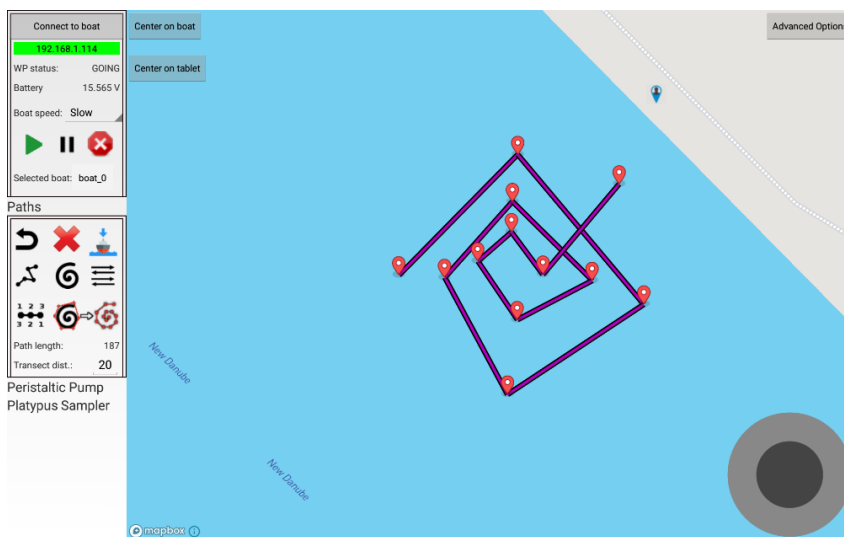


Figure 26: Tablet view with the inserted route for the boat.

With the start button (green arrowhead) displayed in Figure 26 the boat is moving on the desired path. After a measurement has been carried out, the boat is brought back to the shore using the home function.

In the case that the boat is no longer accessible at one point (Wi-Fi is only suitable for approx. 50m), the boat can be accessed remotely by the movement controller so that the boat can be brought back safely to the shore.

After every measurement, the data from reference device and blue box were copied and stored on the measurement computer. In addition, the data on the "BlueGate" server is

checked whether they have also been sent successfully. The data can now be prepared in the same way as in Chapter 4.2.5. The data on BlueGate is then viewed on the "WAQUIN" website and checked for positioning.

5. Results and discussion

5.1 Indoor Validation

5.1.1 Influence of calibration

Due to the different composition or seasonal changes (Ouyang, et al., 2006; Leifer, et al., 2018) of surface water and wastewater, e.g. in the event of significant industrial discharges, local calibration is required to ensure that the circumstances are correct (Langergraber, et al., 2003). The calculation of parameters itself is then based on calibration algorithms emerged out of the raw spectra in combination with lab reference data which are the critical part of the calibrations. Therefore, the quality of laboratory measurements must be proven to obtain good calibration results (Langergraber, et al., 2004). Hence, the implementation of high-quality calibrations is of particular importance.

To guarantee the robustness of the statistical calculations and accurately predicted results, it is recommended to include at least 18 calibration points, for each water matrix.

As previously described in chapter 0, the validation process of the system consisted of performing in-door trials, simulating a realistic wastewater spilling scenarios. So, it was possible to collect enough samples (with the respective reference analysis values) and use those for the preparation of calibration function. After each in-door trial, nine new values were included in the calculation of a new calibration function. The measured data are recalculated and elaborated with every new calibration generated. In this way, it was possible to compare the quality of calibrations by elaborating the data set of each trial with different calibration functions.

For the estimation of the influence of calibration on measurement accuracy, the following calibrations were created by following the steps from the user's manual from Go-Systemelektronik mentioned in *Table 3* (Go-Systemelektronik, 2010):

Table 3: Detailed information about the calibrations for the validation period

all measurements						
Type	Date	Origin of water	Samples	Trials	wavelength numbers	Description
Calibration 1	18.03.2019	Danube	34	1&4	3	Measurement of 25 samples in trial 1 and 9 in trial 4
Calibration 1.2	18.03.2019	Danube	9	4	2	Measurement of 9 samples from indoor trials
Calibration 2	27.03.2019	Danube & New Danube	65	1&2&4&5&6&F1&F2	3	from indoor and outdoor trials
Calibration 3	27.03.2019	Danube & New Danube	31	4&5&6&F1&F2	3	each indoor trial and 2 each field trial
Calibration 4	18.04.2019	Danube & New Danube	42	4&5&6&7&F1&F2&F3	3	and outdoor trials after the fourth trial
Calibration 5	24.04.2019	Danube	36	4&5&6&7	3	Calibrations with only indoor trials after the fourth one

As mentioned, the quality of the calibration implemented on the integrated system may influence the accuracy of the measured data with the BlueScan device. For that reason, the influence of calibration on the accuracy of measured data is an crucial part of the validation procedure, and one example can be seen in Figure 27.

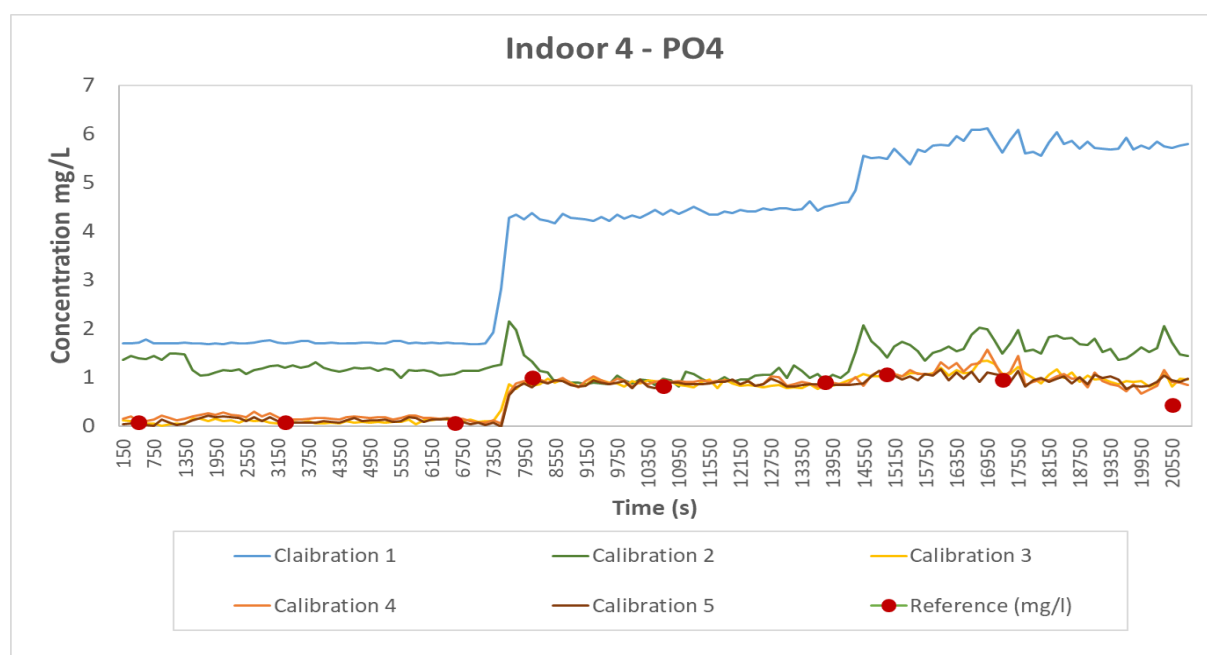


Figure 27: Comparison of reference values and the concentration values of PO4 (mg/L) measured by BlueScan and elaborated with five different calibrations for the data set of trial 4.

Figure 27 shows the results of PO4 concentration, measured with the UV/VIS spectrometer and elaborated with five different calibrations, in comparison with the “true values” obtained from reference analysis (red dots). It can be seen that the most accurate

results are achieved using the calibration no.5, where only indoor measurements are taken into account for the calibration. The reason is that the calibration has enough samples (36), three wavelength and a constant water matrix.

Local calibration

In addition, local calibration can only be used in river basins in the same catchment area, since the change in the so-called water matrix means that the measured values are incorrect.

Spectral quality Index (SQI)

On the other hand it exists the possibility to check the reliability of each single measurement, using a purely qualitative term calculated from the spectral analyser (Mühl, 2012). This so-called spectral quality index (SQI) is saved for every measurement (Fernández, et al., 2018) and gives an indication how well the spectra of the unknown sample fits to that of calibration standards. When the SQI is below 3.5 it indicates a 95% reliability in the measurement value. With an SQI between 3.5 and 4, the reliability decreases to 90%, but if the value is higher than 4 the method is no longer statistically proven (Go-Systemelektronik GmbH, 2019).

Figure 28 shows the influence of calibration function on the SQI value. The first graphic (left) shows the SQI of phosphate measurement with calibrations where only a few samples were used (9 samples), almost after the first measurement. In contrast, there is a calibration with four measurements (36 samples) carried out in the second graphic (right). The orange line is showing the value of 4, from which the measured value is no longer statistically correct.

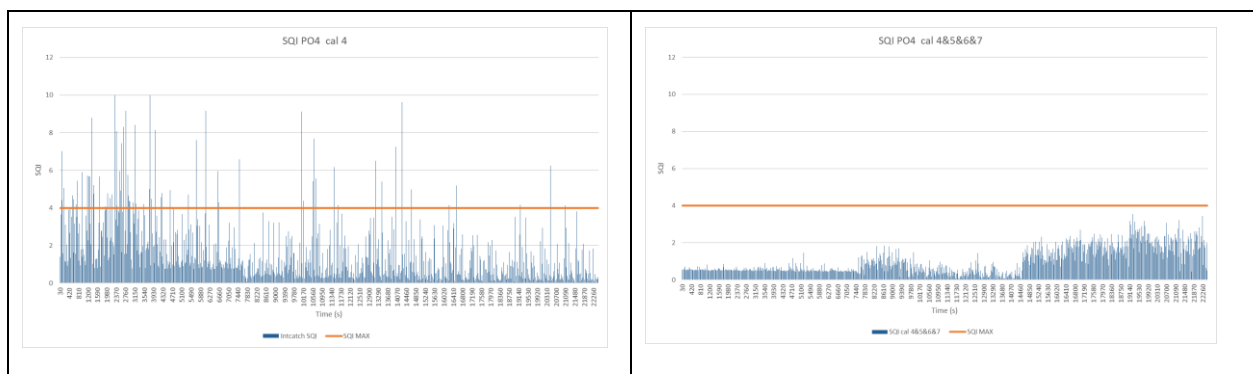


Figure 28: Comparison of the SQI of the measurement of PO4 with different Calibration sets (left: SQI with Calibration 1.2; right: SQI with Calibration 5)

It can therefore be shown that the measurement of an unknown sample of a water body is much more reliable due to more calibration samples, covering a longer period of time and so that more variability on water quality. Therefore calibration 5 seems to be the best for the further validation process.

Finally, it can be concluded that the reliability and accuracy of the predicted data strongly depend on the quality of the calibration function used.

5.1.2 Probes (DO, pH, EC)

As described in chapter 3 the integrated system was equipped with a set of three probes able to measure dissolved oxygen (DO), pH and electrical conductivity (EC).

The Tables below which are presented for each parameter have the column [n] who stands for the number of experiments which were made. They were calculated from values measured every 5 seconds throughout 120min (previously averaged over five values). This means that behind all calculations, stands a total number of approx. 1140 measurements. The measurements of lowest detectable change and repeatability are both measured for the low and high values mentioned in chapter 0. Furthermore, two diagrams are shown after each table in order to better illustrate the result and to improve understanding.

Limit of detection (LOD) & Limit of quantification (LOQ)

The LOD and LOQ results are presented in Table 4. As mentioned in chapter 4.1 the electric conductivity is measured by an inductive measurement which is strongly influenced from existing electrical fields around. This problem was identified early during the indoor trials and could be minimized using an additional grounding of the water tank. Without this grounding, spontaneous fluctuations will appear which leads to high standard deviations and to a higher LOD and LOQ as well. However, the electrical conductivity in surface waters is between 100 μ S and 7mS (Connelly, 2017). This demonstrates that the limit of detection / quantification achieved with the described system is sufficient to allow an appropriate measurement of conductivity in surface water.

Table 4: Mean values of LOD and LOQ of four in-door simulation trials for electrical conductivity, pH and dissolved oxygen, measured with the sensors integrated on the system.

	LOD	% RSD	n	LOQ	% RSD	n
EC ($\mu\text{S}/\text{cm}$)	40	40	4	132	40	4
pH (--)	0.1	55	4	0.5	55	4
DO (mg/L)	1.0	23	4	3.3	23	4

Figure 29 represents two examples of the values calculated for Limit of Detection and Limit of Quantification for parameters pH and dissolved oxygen, obtained through continuous measurements during four different in-door simulation trials. Each bar represents the LOD (darker shade) value calculated as the measurement of the non-spiked sample (lowest in concentration) throughout 120min. The LOQ (lighter shade) value is as well the measurement of non-spiked samples (lowest in concentration) for 120min.

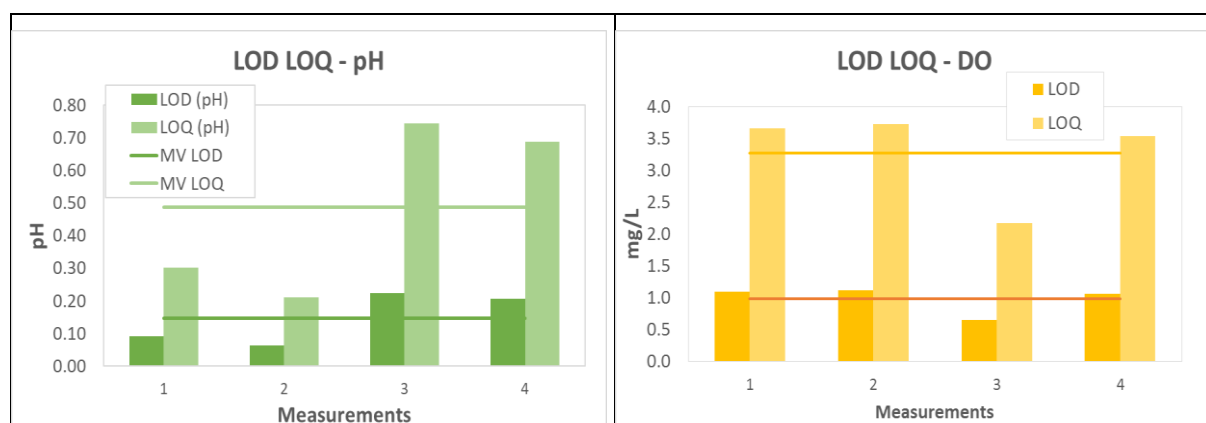


Figure 29: LOD and LOQ values of pH (--) and dissolved oxygen (mg/L) calculated from four different in-door simulations.

The Limit of detection and quantification of EC in comparison with the other probes relatively high, but because of the high measurement range it is acceptable and can be used properly.

Lowest detectable change

The LDC “low” (spike 0) and “high” values (spike 2) in Table 5 represent the mean value of the experiments. The values for the low range are demonstrably too high. This can be explained by the sensor structure and the associated grounding errors described in the paragraph before. Nevertheless, this value is not sustainable and was further improved in the course of the measurements but could no longer be shown in the validation.

Table 5: Mean values of LDC lowest and LDC highest of four in-door simulation trials of electrical conductivity, pH and dissolved oxygen, measured with the sensors integrated on the system.

	LDC (low)	% RSD	n	LDC (high)	% RSD	n
EC ($\mu\text{S}/\text{cm}$)	40	40	4	9	70	4
pH (--)	0.15	55	4	0.05	55	4
DO (mg/L)	1.0	23	4	1.2	66	4

Four validation measurements were carried out for the LDC which are described in Figure 30. The LDC low is displayed as darker shade and the high as a lighter shade. On the first look on the results of the pH measurement it seems that there is a big difference between the first two measurements and the rest, but with a closer look it is possible to see that the difference is only about 0.1 pH values which is viable for the measurement system

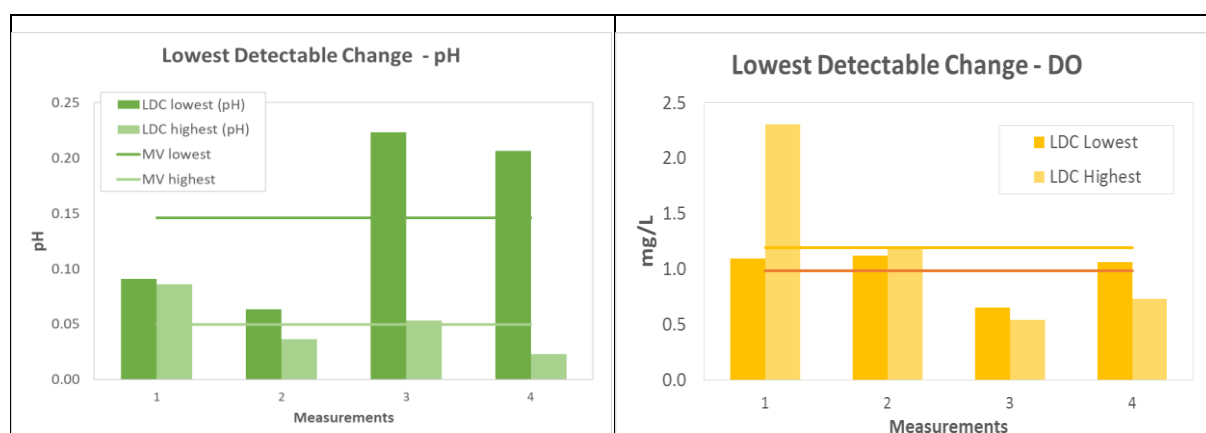


Figure 30: LDC low and LDC high values of pH (--) and dissolved oxygen (mg/L) calculated from the data of four different in-door simulations.

In order to be able to complete this part, it must be noted that this measurement shows that the measurement of the electric conductivity becomes more precise with increasing pollution. Furthermore, it can be said that the change in the measurement of pH and dissolved oxygen does not show any major changes when the wastewater concentration is increased

Repeatability

Table 6 indicates the repeatability “low” (spike 0) and the “high” values (spike 2). The repeatability shows the precision of the measurements. Since the measurement of the electrical conductivity lies in a range far above the limit of quantification ($350\mu\text{S}$), the measurement is comparatively as stable as the rest of the measurements.

Table 6: Validation results for repeatability given in % (lowest and highest) of four in-door simulation trials for electrical conductivity, pH and dissolved oxygen.

	Repeatability % (low)	% RSD	n	Repeatability % (high)	% RSD	n
EC	3.3	28	4	0.6	54	4
pH	0.6	55	4	0.2	55	4
DO	3.0	19	4	5.5	81	4

The repeatability of the measurement of EC, pH, and DO is in all cases < 5.5% and this indicates an outstanding measurement precision for these parameters.

In *Figure 31* the values are also displayed in a lighter shade for high values and a darker shade for lower values. It can be mentioned that the lower values for electric conductivity measurement have a higher repeatability percentage than with the higher values. Nevertheless, these values are precise enough for the system as they are not higher than the other repeatability measurements.

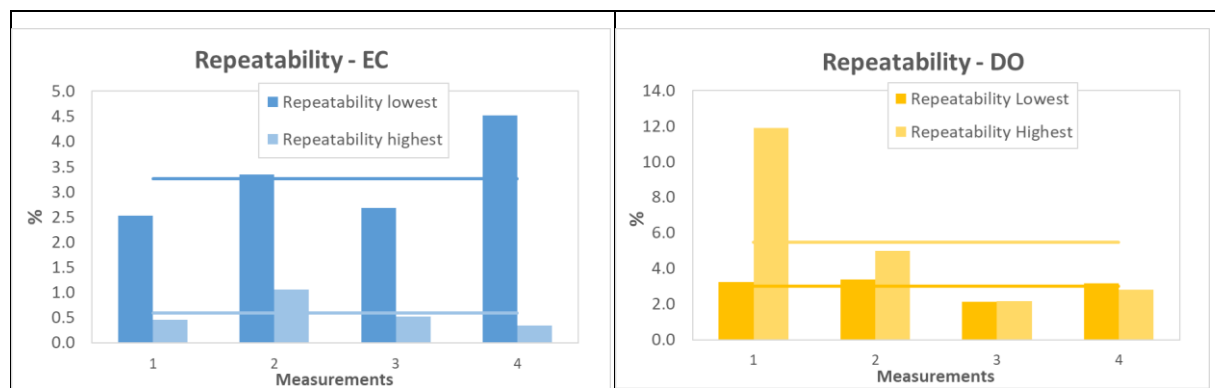


Figure 31: Repeatability lowest and highest values of electrical conductivity and dissolved oxygen calculated from the data of four different in-door simulations.

Accuracy

The results of this validation work are presented in *Table 7*. All measurements are split among three spikes where the accuracies of all measurements were tested.

Table 7: Mean and RSD values of accuracy for electrical conductivity, pH and dissolved oxygen, measured with the sensors integrated on the system, during four in-door simulation trials.

		Accuracy (%)	% RSD	n
EC	Spike 0	96	29	4
	Spike 1	89	28	4
	Spike 2	91	29	4
pH	Spike 0	101	1	4
	Spike 1	102	1	4
	Spike 2	102	1	4
DO	Spike 0	99	4	4
	Spike 1	95	7	4
	Spike 2	94	7	4

The validated accuracy values presented very good values (89 – 102%) for all selected probes in the integrated system.

Figure 32 represents the values calculated for the accuracy of the parameters pH and dissolved oxygen measured during measurements carried out in four different in-door simulation trials. Each bar represents the accuracy (darker shade) value calculated as % recovery of the values of the non-spiked samples (lowest in concentration) compared to the reference values, and they represent the accuracy (middle shade) value calculated as % recovery of the values of the first level of the spiked sample, and finally, the accuracy (lighter shade) value calculated as % recovery of the values of the second level of the spiked sample (highest in concentration) compared to the reference values.

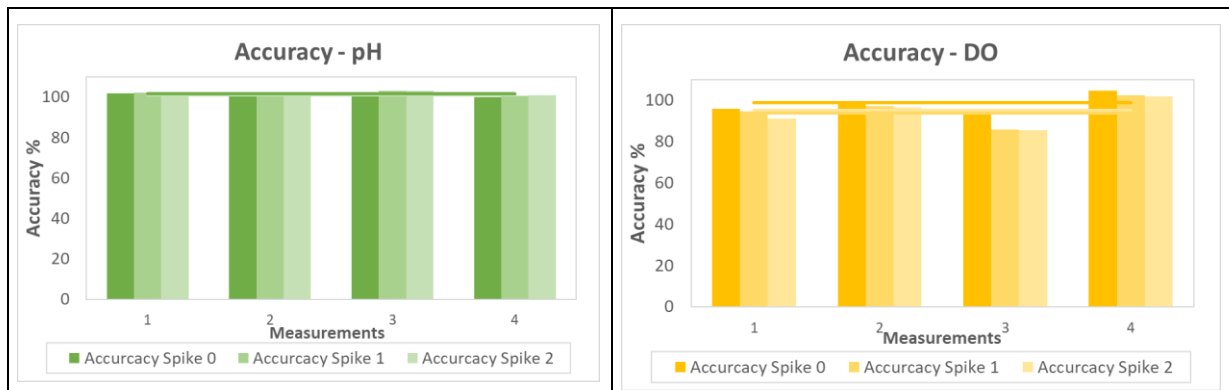


Figure 32: Accuracy (Recovery in %) of pH and dissolved oxygen, calculated from the data of each of the spiking level of four different in-door simulations.

The measurements of the probes are working quite well, only the electric conductivity has difficulties with the environment due to electrical fields which influence the measurement. To overcome this problem, many grounding checks were made, as described in chapter 0. However, all measurements are working good in their working range and show good accuracy.

5.1.3 In-Situ Spectrum Analyser (Spectrometer)

The values in this tables below represent the mean value of three or four experiments ($n=3$ or 4), each of them calculated from values measured every 30 seconds for 120min (previously averaged over five values). That means, that behind each of these mean values a total number of approx. two hundred measurements (or a total of ~150 measurements, for $n=3$) were combined. Also, the measurements for lowest detectable change and repeatability were done with low and high values as mentioned in chapter 0. Furthermore, as well as in these chapter two diagrams are shown after each table in order to better illustrate the result and to improve understanding.

Limit of detection and Limit of quantification

The results of LOD and LOQ of this validation work are presented in *Table 8*.

Table 8: Mean values of LOD and LOQ of four in-door simulation trials of BOD₅, COD, NH₄, NO₃, PO₄, TOC and Turbidity.

	LOD	% RSD	n	LOQ	% RSD	n
BOD ₅ (mg/L O ₂)	1.7	6	4	5.8	6	4
COD (mg/L O ₂)	4.1	28	4	14	28	4
NH ₄ (mg/L NH ₄)	0.5	23	4	1.7	23	4
NO ₃ (mg/L NO ₃)	0.1	76	4	0.5	76	4
PO ₄ (mg/L PO ₄)	0.2	13	4	0.6	13	4
TOC (mg/L C)	2.3	43	4	7.8	43	4
Turbidity (NTU)	39	25	3	129	25	3

These results show the limit of quantification and the limit of detection of the measurement, which are determined as described in Chapter 4.2.4. To quantify the results, the quality target regulation for chemistry must be used (Bundesministerium für Land- und Forstwirtschaft, 2009). As an example, the BOD₅ value in the Danube should not exceed the value of 3,5 mg/l O₂ that the status of very good water quality can be maintained. Looking at the validation results it is possible to detect this with the system. However, the measurement of phosphate, ammonia and turbidity cannot measure values in the measurement range where the water quality limits are stated. Nevertheless, the purpose of monitoring can be guaranteed as this system can measure contamination peaks of wastewater discharges as it is needed for the use mentioned in chapter 3. If a

more precise measurement for lower concentrations is necessary, other sensors such as the ion-selective sensors must be used (WTW GmbH, not dated).

Figure 33 represents an example of the values calculated for Limit of Detection and for Limit of Quantification of the selected parameters Biological oxygen demand and ammonia. Each bar represents the LOD (darker shade) value of the non-spiked samples (lowest in concentration); and LOQ (lighter shade) value as well of the non-spiked samples (lowest in concentration).

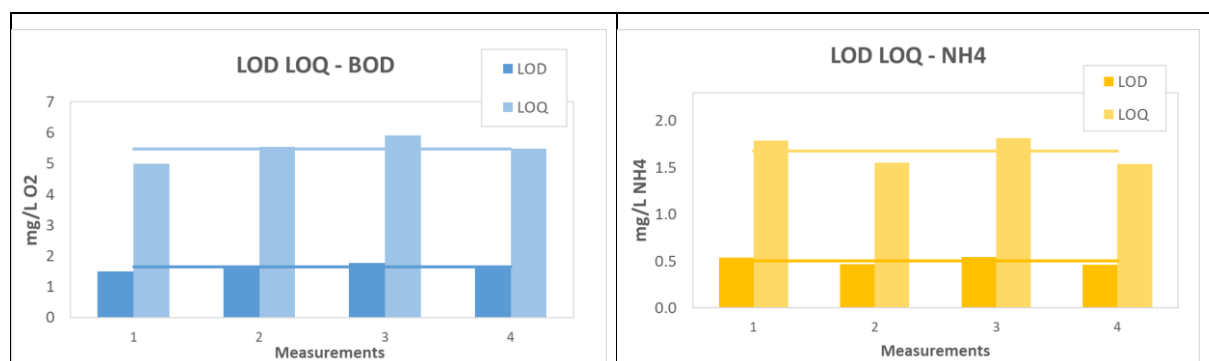


Figure 33: LOD and LOQ values of BOD₅ (mg/L O₂) and NH₄ (mg/L NH₄) calculated from four different in-door simulations.

Lowest detectable change

The LDC low (spike 0) and LDC high (spike 2) are calculated and presented in Table 9.

Table 9: Mean values of LDC lowest and highest of BOD₅, COD, NH₄, NO₃, PO₄, TOC and Turbidity, measured during the four in-door simulation trials.

	LDC (low)	% RSD	n	LDC (high)	% RSD	n
BOD ₅ (mg/L O ₂)	1.7	6	4	3.4	45	4
COD (mg/L O ₂)	4.1	28	4	20	47	4
NH ₄ (mg/L NH ₄)	0.5	23	4	2.4	67	4
NO ₃ (mg/L NO ₃)	0.1	76	4	0.9	112	4
PO ₄ (mg/L PO ₄)	0.2	13	4	0.4	56	4
TOC (mg/L C)	2.3	43	4	5.5	55	4
Turbidity (NTU)	54	60	4	54	44	4

With rising contamination, the Limit of detection is also rising but, in a range, where the system can obtain a reliable measurement.

Figure 34 represents the values calculated for the lowest detectable change of the selected parameters Chemical oxygen demand and phosphate. The bars represent the

LDC lowest (darker shade) value, and LDC highest (lighter shade) value of the second spiking level samples (highest in concentration).

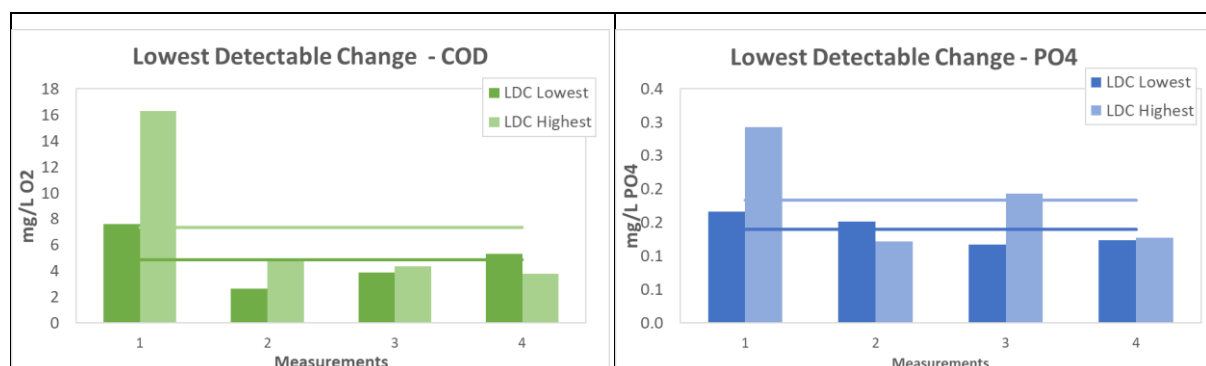


Figure 34: LDC lowest and highest values of COD (mg/L O₂) and PO₄ (mg/L PO₄) calculated from four different in-door simulations.

With these figures, the statement below the table can be verified. The mean value of the higher contaminated spike is higher than the lower concentrated one.

Repeatability

The repeatability low (spike 0) and high (spike 2) values are presented in Table 10.

Table 10: Mean values of Repeatability low and high of three or four in-door simulation trials of BOD₅, COD, NH₄, NO₃, PO₄, TOC and Turbidity.

	Repeatability (low) [%]	% RSD	n	Repeatability (high) [%]	% RSD	n
BOD ₅	37	37	4	6	22	4
COD	15	47	4	4	30	4
NH ₄	48	30	3	5	49	3
NO ₃	0.7	72	4	4	132	4
PO ₄	49	37	4	9	40	4
TOC	20	42	4	7	59	4
Turbidity	20	58	3	14	23	3

The validated values presented in this table show that the repeatability of the listed parameters, calculated for the concentration of spike 2 (high), which is more representative for real cases, is less than 10%, besides of turbidity (14%). This indicates an exquisite measurement precision for these parameters.

Figure 35 represents the values calculated for repeatability of the selected parameters ammonia and turbidity. Mentioned is the repeatability low (darker shade) value and repeatability high (lighter shade) value.

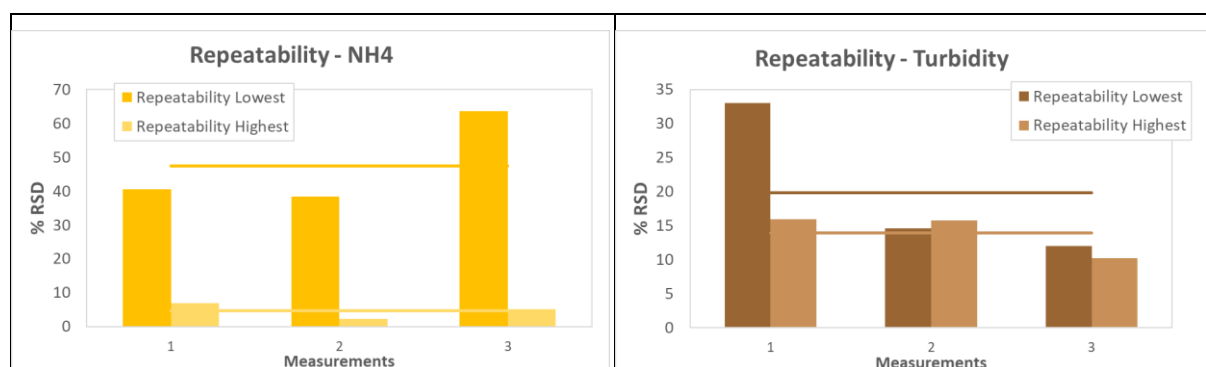


Figure 35: Repeatability lowest and highest values of NH₄ (mg/L NH₄) and Turbidity (NTU) calculated from three different in-door simulations

The difference between the mean value of the highest and lowest repeatability of ammonia can be described with the concentration that was measured. In spike 0 (low) the values were below the limit of detection in contrast with spike 2 (high) the values were above the limit of quantification which automatically should lead to this outcome.

Accuracy

The results of this validation work are presented in Table 11. The accuracy is separated for all measured values in the three spikes.

Table 11: Mean values of the accuracy of BOD₅, COD, NH₄, NO₃, PO₄, TOC and Turbidity, measured during the four in-door simulation trials.

		Accuracy (%)	% RSD	n
BOD ₅	Spike0	(139)	44	4
	Spike1	106	13	
	Spike2	101	18	
COD	Spike0	(100)	17	4
	Spike1	105	5	
	Spike2	101	4	
NH ₄	Spike0	(343)	115	4
	Spike1	103	17	
	Spike2	91	11	
NO ₃	Spike0	(100)	2	4
	Spike1	97	3	
	Spike2	104	6	
PO ₄	Spike0	(168)	63	4
	Spike1	95	11	
	Spike2	97	17	
TOC	Spike0	(101)	21	4
	Spike1	101	5	
	Spike2	109	18	
Turbidity	Spike0	(151)	73	3
	Spike1	85	30	
	Spike2	96	20	

The accuracy values of “spike 0” are not considered, as the concentration measured is, in most cases lower than LOD. The validated values presented in the table show an excellent performance of the selected probes regarding accuracy.

Figure 36 represents an example of accuracy for the selected parameters COD, and NO₃. The accuracy value calculated of the spikes are displayed in the graphs.

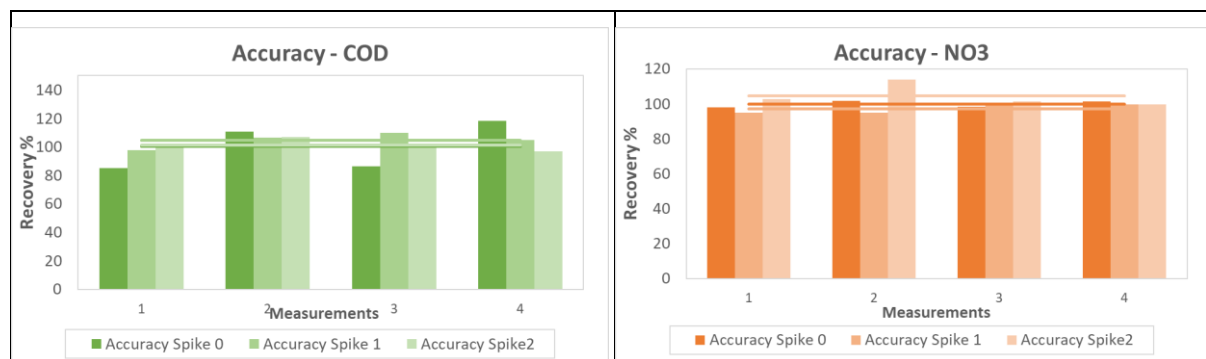


Figure 36: Accuracy values of COD (mg/L O₂) and NO₃ (mg/L NO₃) calculated from four different in-door simulations.

To mention the outcome of the validation for the spectrometer it can be said that the required performance could be met. Just as with the probes, an improvement in the accuracy with increasing the concentration was found. This can be described based on the values at Spike 0 which are below the limit of detection.

5.2 Outdoor validation

Interaction of the components in the integrated system

The goal of this validation part is to observe interactions among the components of the integrated system (autonomous control unit, mobile phone, BlueBox and BlueGate) during its working procedure. The autonomous driving mode of the integrated system was tested by using the Control GUI and its functions at three different levels of velocity. As already mentioned, the range for controlling the boat is limited to 100 m, but the autonomous mode worked with the programmed route even outside this range. The transfer of data from the BlueBox to the BlueGate succeeded during the driving tests. It was possible to download the data from BlueBox and to visualise them on the cloud (BlueGate).

Movement controller as a backup function

In this section, the interaction of the backup movement controller with the integrated system by overriding the autonomous control unit and manually driving the boat is assessed. It turned out that the connection between this controller and the integrated system is working well up to 100m distance from user.

Data mapping

The primary purpose of this topic is to check the data visualisation using WAQUIN and WAIS app. It was possible to display the selected catchments for the created campaign and the measured concentrations of chemical parameters into WAQUIN. In Figure 37 and Figure 38 is shown the path of the autonomous boat during a measuring campaign. The points represent the results of every single measurement for the specified parameter (TOC and pH), coloured according to the legend.

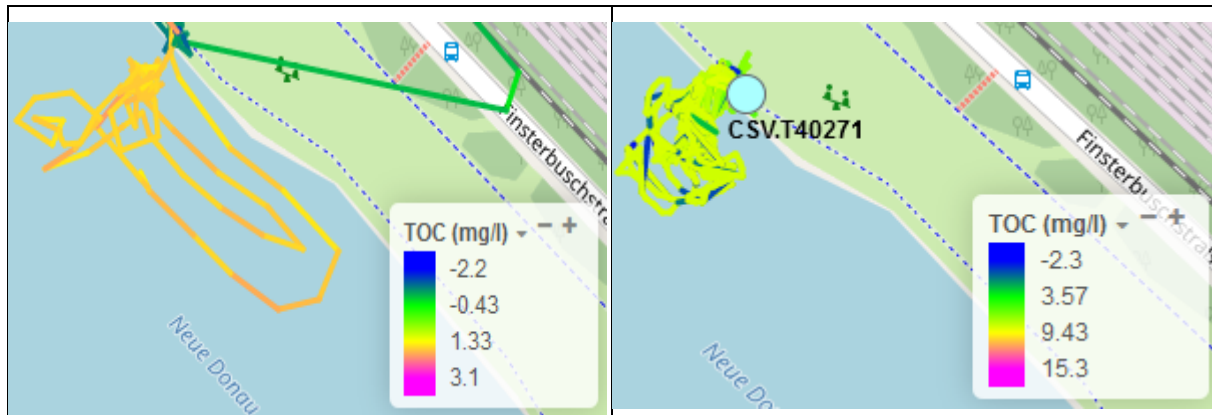


Figure 37: WAQUIN map (Basemap) with TOC-data (left: outdoor test 2, right: outdoor test 3).

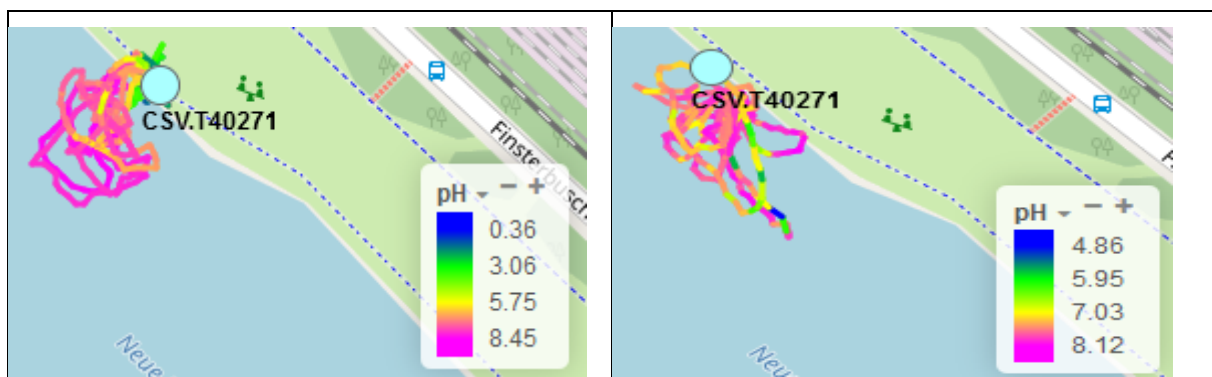


Figure 38: WAQUIN map (Basemap) with pH-data (left: outdoor trial 3, right: outdoor trial 4).

Measurements with the probes and the spectrometer

The measurements were carried out with the calibrations from the indoor trials. But there was a very big difference between the reference values and the measurements from the boat. The reason for this is the changed water matrix and the few measurements with very low contamination. A possible solution in order to be able to carry out measurements at this location lies in the calibration, which has to be created again.

5.3 Performance Characteristics

After the whole validation process the data need to be evaluated as a complete table shown in *Table 12*.

Table 12: Performance Characteristics of the Boat Sensors for BOD₅, COD, NH₄, NO₃, PO₄, TOC Turbidity, EC, pH and DO, measured all trials.

	LOD	LOQ	LDC	Repeatability (%)	Accuracy (%)
BOD ₅ (mg/L O ₂)	1.7	5.8	1.7 - 3.4	6 - 37	101 - 106
COD (mg/L O ₂)	4.1	14	4.1 - 20	4 - 15	101 - 105
NH ₄ (mg/L NH ₄)	0.5	1.7	0.5 - 2.4	5 - 48	91 - 103
NO ₃ (mg/L NO ₃)	0.1	0.5	0.1 - 0.9	0.7 - 4	97 - 104
PO ₄ (mg/L PO ₄)	0.2	0.6	0.2 - 0.4	9 - 49	95 - 97
TOC (mg/L C)	2.3	7.8	2.3 - 5.5	7 - 20	101 - 109
Turbidity (NTU)	39	129	54	14 - 20	85 - 96
EC (μS/cm)	40	132	9 - 40	0.6 - 3.3	89 - 96
pH (–)	0.10	0.50	0.05 - 0.15	0.2 - 0.06	101 - 102
DO (mg/L)	1.0	3.3	1.0 - 1.2	3.0 - 5.5	94 - 99

All values from the previous measurements were inserted in this table in order to obtain a targeted overview of the performance of the system. Now it is possible to submit evaluations that were made possible by the validation.

5.4 Discussion of the research questions

1. **What is the effort required for the calibration of the sensors?**

At the beginning of the work a global calibration can be used. This calibration cannot really be used with regard to the accuracy of the specified measurement. Because of that the use of a local calibration is necessary. The first step is to make measurements with the boat and additionally take samples for a laboratory analysis. In chapter 5.1.1 five different calibrations are described. In the second step these calibrations are compared to the reference values of a measurement. It was found that the last three calibrations 3 - 5 correspond most exactly with the reference values. In conclusion Calibration 5 was then used for the validation since this measure the reference values most precisely.

2. **How robust are the calibrations of the sensors in relation to other water matrices?**

As described before, the global calibration can sometimes produce wrong values for specific water bodies. A local calibration which is in this case required can then only be used for a specific river section as described in chapter 3.6. As an example, if the same calibration is used for a water body that has a different water matrix, the calibration is invalid and must be created again. In chapter 5.2, this difference was also recognized in the field trials, since the calibration did not show the correct results.

3. **How the validation process has to be carried out so that the field conditions are adequately described?**

That a validation can best represent the field conditions, the measurements must be carried out according to the international standard as described in chapter 4.2.1. The results can then be used to create an adequate description. With this so-called Performance Characteristics another table to describe the power of the measurement can be made. It contains the performance characteristics of LOD and accuracy of each measurement parameter. These two characteristics are then combined as a performance rating of each measurement shown in Chapter 6.

4. Is it possible to measure parameters describing eutrophication with an on-line UV/VIS – Spectrometer?

For this purpose, the table in chapter 5.3 is compared with the table in chapter 3.2. It can be determined that the limit of detection for ammonia is 0.5 mg/l, which is in the middle range compared to the limit values, since the limit value is set between 0.4 and 0.6 mg/l. For phosphate, the limit of detection is 0.2 mg / l, which is comparatively more likely to be in the upper range of the limit values, since this is set between 0.07 and 0.2 mg / l. Overall the result of this measurement was particularly gratifying, since they showed good results in relation to the performance rating.

5. Is the integrated system capable to detect wastewater spills?

To answer this question, it must be determined that wastewater consists of organic contaminants, which are listed in section 3.2. Possible indicators would then be DO, BOD₅, COD and ammonium. If these values are compared again with the table in chapter 3.2 and with the table in chapter 5.3, it can be determined that the limits of detection for the measured quantities are below the limit values except for ammonium which is described in the previous answer. The detection limit for BOD₅ is 1.7 mg/l and the limiting value is 4-6 mg/l. For DO the limit of detection is 1.0 mg/l O₂ which is as well below the limit value of 8-12 mg/l O₂. COD with a limit of detection of 4.1 mg/l O₂ is also below the limit value of 7-10 mg/l O₂. Overall, the integrated system can detect spilled wastewater with excellent performance.

6. Conclusion and outlook

The main objective of this thesis was the validation of the performance of the system which is stated with a European project by making indoor and outdoor trials. This chapter connects the results of the objectives and shows an outlook for further projects. The search for the parameters that are necessary for the observation or quantification of surface waters could be found very quickly since they are laid down both in the Quality Target Ordinance for Chemistry in Surface Waters and the Water Framework Directive. After online monitoring has been used in many cases (measuring buoys, measuring boats) (Niclos, et al., 2005), a quick decision about the usefulness of this system could be made. As mentioned at the beginning, eutrophication is becoming a problem for water quality. In order to recognize this problem early on, the parameters ammonium and phosphate must also be monitored. However, this monitoring is still relatively new and is only offered by a few companies. Because of this, the spectrometer from Go-Systemelektronik was used. Ratification of the measured parameters was carried out in *Table 13*.

Table 13: Rating of the system with its detection and accuracy to get the performance evaluation for the indoor trials (detection: + = can detect the contamination in the tolerance limits, +/- = is capable to detect wastewater spills; accuracy: + = 95 - 100%, +/- = 90 - 95%, ~ = 90 - 85%; performance: depend on the previous rating)

	Detection	Accuracy	Performance
BOD ₅ (mg/L O ₂)	+	+	+
COD (mg/L O ₂)	~/+	+	+
NH ₄ (mg/L NH ₄)	~/+	~/+	~/+
NO ₃ (mg/L NO ₃)	+	+	+
PO ₄ (mg/L PO ₄)	~/+	+	+
TOC (mg/L C)	+	~/+	+
Turbidity (NTU)	~/+	~	~/+
EC (μS/cm)	+	~	~/+
pH (--)	+	+	+
DO (mg/L)	+	+	+

The problems of measuring electrical conductivity can also be seen here. However, the measurement of the turbidity also has problems which can be attributed to the

spectrometer and a bad calibration which was sorted out at the end of the validation. The measurement of the eutrophication parameters can be classified as good to very good. The remaining parameters can be quantified in a similar way and thus show that the measurement can be used for the purpose of detecting the effects of wastewater in surface waters. However, it must be noted that these results could only be achieved by analysing the calibrations. The calibration used has a major impact on the results. It is important to make calibrations only with the water samples where the boat is used. This is the reason for the measurement environment where the system can be used. It is not possible to measure an area where no local calibrations were made with this boat.

Overall, however, it can be said that the goals, in particular the detection of wastewater flows, could be proven. However, it should be noted that the system cannot deliver very precise results. This can partly be explained by the increased detection limit or also due to measurement problems. Good monitoring is ensured in particular in the case of discharges of wastewater, which can thus be specifically identified. This warning can then be forwarded to the Ministry of the Environment, for example. However, sampling must be carried out for confirmation.

Shortly after the work was completed, the research boat was transferred to Spain, where it was taken over by the university for further testing. Also, further boats of this type will be developed in the future, as this project was the review of the system. It was planned to complete the INTCATCH project by the year 2020 and to be ready for development and research. However, not all functions have been thoroughly tested. Such as the analysis of microbiological data to detect faecal indicator bacteria such as *Escherichia. Coli* and enterococci (Lim, et al., 2017) by a DNA measurement; the project is most probably still going on. Also, the grounding problems with the EC measurement can be improved like they are shown in chapter 0 or the changing from an inductive measurement to a conductive could be a solution.

Nevertheless, this topic has become an absolute success, as many new variants have been tested and applied. However, until it comes to the fact that one of these boats will be launched on the market probably five years pass. Then it will be possible for small companies, NGOs communities to check their water sections for illegal discharges of wastewater and to take measures.

7. Summary

When the Water Framework Directive was introduced in the European Union in 2000, the biggest goal was to expand the scope of water protection to all waters and achieving “good status” for all waters set by a deadline. This was necessary because many cities draw their drinking water from surface waters. To achieve this, nationwide surveillance had to be implemented. For the detection of the flow, the speed and the depth systems were already developed, which could capture long-term data. However, the quality of the water can still only be measured in a snapshot by sampling and laboratory.

The European Union funded INTCATCH project (which stands for "Integrated Tools for Monitoring and Managing Catchments") started in the Year 2017. INTCATCH focused on the development, research and marketing of autonomous platforms, mainly intended for estimation of water surface quality and in-situ detection of point and diffuse pollution. One powerful sensor utilised for this purpose is the in-situ UV/VIS spectrometer, which allows the simultaneous measurement of the parameters Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD₅), Total organic carbon (TOC), Nitrate, phosphate, ammonia and turbidity. Additional three probes for the measurement of dissolved oxygen, pH and electric conductivity are included in the overall system.

A specific UV/VIS probe was then installed in an autonomous robotic boat which was additionally equipped with the sensors for pH, dissolved oxygen, electrical conductivity and called integrated system. After the device has been installed and the boat has met all the requirements for autonomous use, one has moved to the step of validation.

The validation is performed according to the international standard ISO 15839:2003(E) and includes two parts, and one part consists of experiments under laboratory (indoor) conditions; the other is carried out in the field (outdoor). In the indoor trials, so-called spikes were performed so that a simulated discharge of three different concentrations of pollution could be analyzed. In this process, river water is initially filled into a tank. In the subsequent spiking steps, the content of wastewater was increased by supplying the influent and effluent of an SBR plant. Subsequently, these tests were carried out every two weeks and each time calibrations were carried out with the reference values from the laboratory.

The outdoor field tests were in the real sense not for the determination of the measured values, but rather for the verification of the functionalities of the boat:

- Signal sender and receiver
 - o Global Positioning System (GPS)
 - o Remote control antenna (RC)
 - o Mobile network
- The autonomous control unit (Tablet)
 - o Base map included
 - o Control graphical user interface (GUI) installed
- The connection between boat and autonomous control unit (Mobile phone)
 - o Compass
 - o Boat server installed
- Movement controller as a backup function
- Data mapping
 - o Measurements with GeoReference
 - o Working with WAQUIN as a platform to display the results of the measurement
 - o Working with WAIS for the interaction with the data server BlueGate
- Water quality probes
 - o DO, EC, pH, UV/VIS spectrometer

Table 14 shows the performance characteristics of the integrated system. It can be seen that the accuracy in all cases except the turbidity is outstanding.

Table 14: Performance characteristics of the integrated system

	LOD	LOQ	LDC	Repeatability (%)	Accuracy (%)
BOD ₅ (mg/L O ₂)	1.7	5.8	1.7 - 3.4	6 - 37	101 - 106
COD (mg/L O ₂)	4.1	14	4.1 - 20	4 - 15	101 - 105
NH ₄ (mg/L NH ₄)	0.5	1.7	0.5 - 2.4	5 - 48	91 - 103
NO ₃ (mg/L NO ₃)	0.1	0.5	0.1 - 0.9	0.7 - 4	97 - 104
PO ₄ (mg/L PO ₄)	0.2	0.6	0.2 - 0.4	9 - 49	95 - 97
TOC (mg/L C)	2.3	7.8	2.3 - 5.5	7 - 20	101 - 109
Turbidity (NTU)	39	129	54	14 - 20	85 - 96
EC (μS/cm)	40	132	9 - 40	0.6 - 3.3	89 - 96
pH (–)	0.10	0.50	0.05 - 0.15	0.2 - 0.06	101 - 102
DO (mg/L)	1.0	3.3	1.0 - 1.2	3.0 - 5.5	94 - 99

All in all, with this validation, the boat could be checked for all minor matters. There were also some difficulties such as grounding and water ingress, which were corrected during the validation. In conclusion, this project was a complete success, and the results achieved can be used for future boats.

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Appendix

Spectrometer difficulties

In the beginning, some difficulties were keeping the intensity of the spectrum constant. The error was found after an exhausting two days search. It was the prism of the spectrometer (BlueScan) which damped the light on the glass surface due to moisture. After an attempt to dry the plastic Prisma insert, tie it with Teflon tape and seal it with silicone and this did not lead to the solution of the problem, an alternative had to be found. Fortunately, weeks ago, an aluminium prism was introduced, which could be delivered to the project and installed within a week. As a result, at least the time lag was kept within limits.

Grounding problems

After a few indoor and outdoor measurements, it was recognised that measuring the pH in the indoor test showed the same value as the reference measurement, but in the outdoor test, this was quite different. The cause of this problem was not resolved until the last phase of the project, as wasting much time on the analysis. In the beginning, we tried to separate the sensors to minimise possible interferences. Nevertheless, this measure has helped only minimally. So, it was thought of the system grounding. Namely, this should lead all parts to zero potential so that no distortions of the measured values take place.

The grounding for the INTCATCH boats is done by a connection between the negative pole of the battery and the water. One way to do this is the connection of the battery with the cooling loop of the engine, which relates to the water.

As it turned out that the grounding has a strong influence on the signal of the EC, pH and DO probes, some optimisation work is performed with the grounding system of the boat, in order to avoid electrical interferences. Four different grounding alternatives were tested.

From the obtained results (pH, EC, DO) the alternative which connects the motor shaft and cooling system with two separated cables was the optimal configuration and therefore chosen for the following tests. Nevertheless, further data accuracy issues appeared again due to wrong grounding connections. For this reason, other grounding tests were carried

out and could be concluded, that a more reliable solution was the grounding alternative shown in Figure 39: Wiring diagram for grounding of the boat T40271 where the used grounding for the last measurements is shown. It starts at the motor shaft, the motor cooling and the negative pole of the battery. The printed circuit board (PCB) needs to be connected on the right spot (see PCB grounding spots on the maps for each Printed circuit board) with the cable coming from the grounding connection with the negative pole of the battery. The next step is to connect this cable also with the DC/DC-converter minus pole. After that, a bypass around the DC/DC- converter is installed.

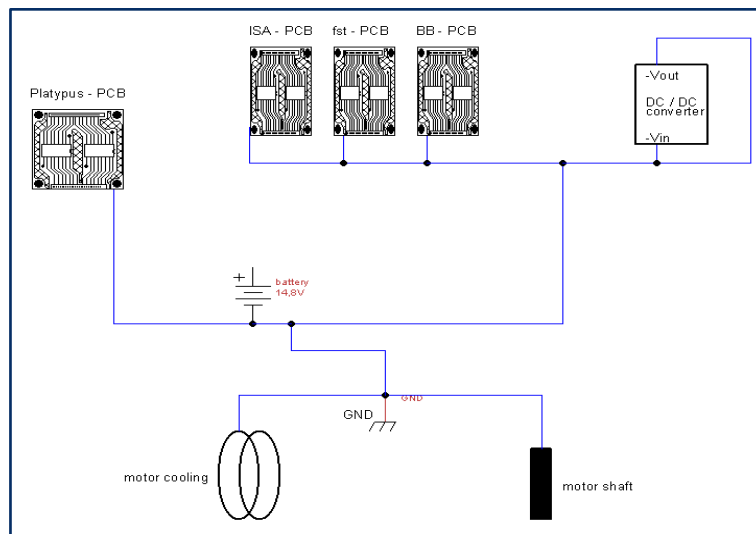


Figure 39: Wiring diagram for grounding of the boat T40271

The application of this grounding configuration led to more accurate results for pH, electric conductivity and dissolved oxygen, as can be seen in Figure 40.

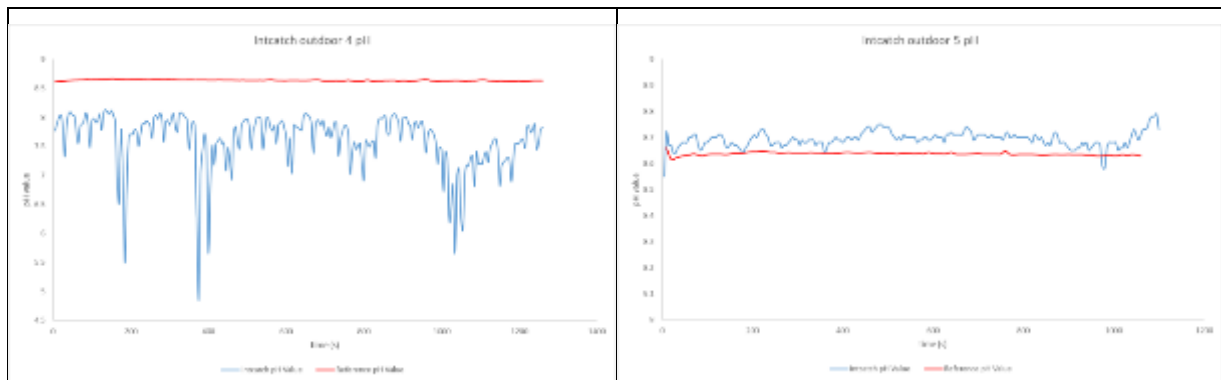


Figure 40: Influence of grounding on measurement accuracy for pH (left: non-optimal grounding; right: grounding according to Figure 39)

Water leak

Coincidentally, water ingress was detected during a test at the technical hall. This was located on the ground in the engine compartment where water was collected. Due to the position of the leak, where both the battery and the drive of the boat are held, the attempt was aborted, and the troubleshooting started. The first possible point was the cooling spiral on the underside, as shown in Figure 41.



Figure 41: Cooling spiral on the bottom side of the boat to cool the engines in the engine compartment

However, after closer inspection, it was recognised that the openings in the inside were sealed very well.

The fault was subsequently discovered at the back, namely at the points where the motor shaft leads to the rotors. The fear at the beginning was that the water in the motor shaft, that is promoted by the motor shaft in the boat. Nevertheless, the hope was that water would only enter the outside of the motor shaft.

So, it was started with the removal of the old silicone. Thereby vacancies were found which caused the first glimmer of hope not to have to disassemble the whole boat.



Figure 42: Engine shaft at the rear side of the boat (l. after removing the old silicone, r. after putting acryl on it)

Subsequently, a layer of acrylic was placed around the shaft, which should ultimately seal the open watertight. After 24 hours, the boat was subjected to an intensive test. It was given at the beginning for an hour in the trial tank and waited for whether a water entry takes place. After this time, no water was spotted in the engine compartment, which started the second test. Both engines have been put into operation. After this endurance test also led to no water entry could be confirmed with certainty that the problem has been eliminated.



Figure 43: Boat in the trial tank for the second test with running engines

Turbidity measurement

The measurement of turbidity was a challenge for the spectrometer. Initially, only synthetic calibrations were available for validation, which was useful only for the specific case of given synthetic turbidity. Subsequently, a new calibration was performed in each measurement, but since the Danube water was significantly different in the months of the study due to, e.g. Flood, low water, regular water, no continuous calibration could be carried out. Furthermore, the circumstance of the measurement with the spectrometer without a 90° offset nephelometric detector also plays a significant role as described in chapter 5.1.3.

Measurement of Phosphorus and Ammonia

One of the significant issues in the investigation was whether it is possible to detect phosphate and ammonium by this spectroscopy. This test went very well with the spectrometer on the boat. The measurements nearly met the reference values after the required reference sample quantity was available for complete calibration.

However, in the measurements for the mobile ISA, a few findings were made after the measurement did not meet the reference:

- The matrix (Danube) must not be changed
- The calibration must match the measured matrix
- The turbidity must not be too high
- The cleaning of the ISA must be done properly

PO₄ causes more, more significant changes in the spectra. This is due to the more stable phosphate compounds against temperature effects, light effects. Experience has shown that even for a good/stable PO₄ calibration, fewer reference values/samples are needed than for an NH₄ calibration.

Mentioned in the next figures are measurements described in the figure title. In these measurements, the steps from the spiking process can be well recognized.

The BOD₅ level shown in *Figure 44* describes an increase in the value if the contamination is increased.

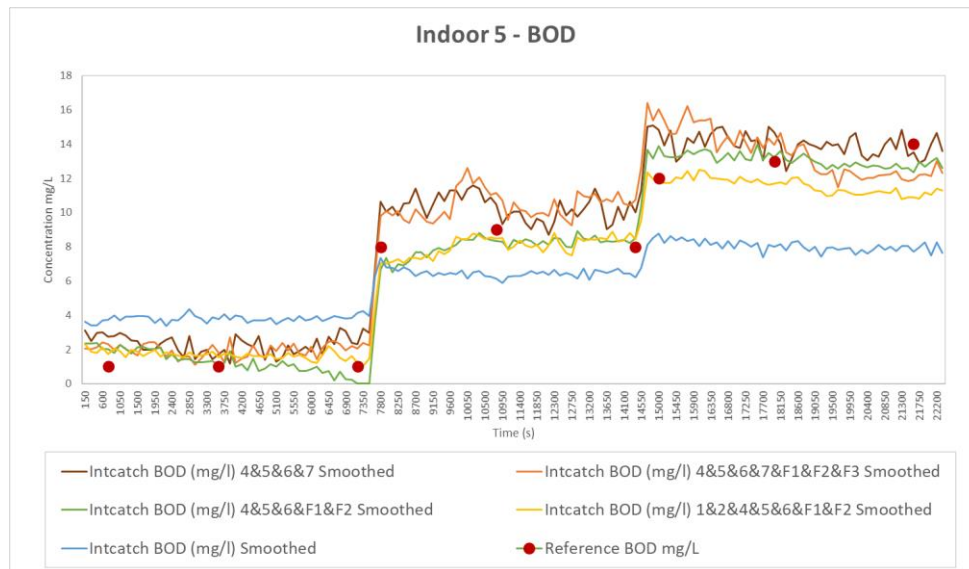


Figure 44: BOD₅ measurement of indoor trial 5 with five calibrations with the reference points of the laboratory measurement

In Figure 45 the measurement of ammonia is displayed. There is a rise in the concentration like before with BOD₅ when the contamination is increased.

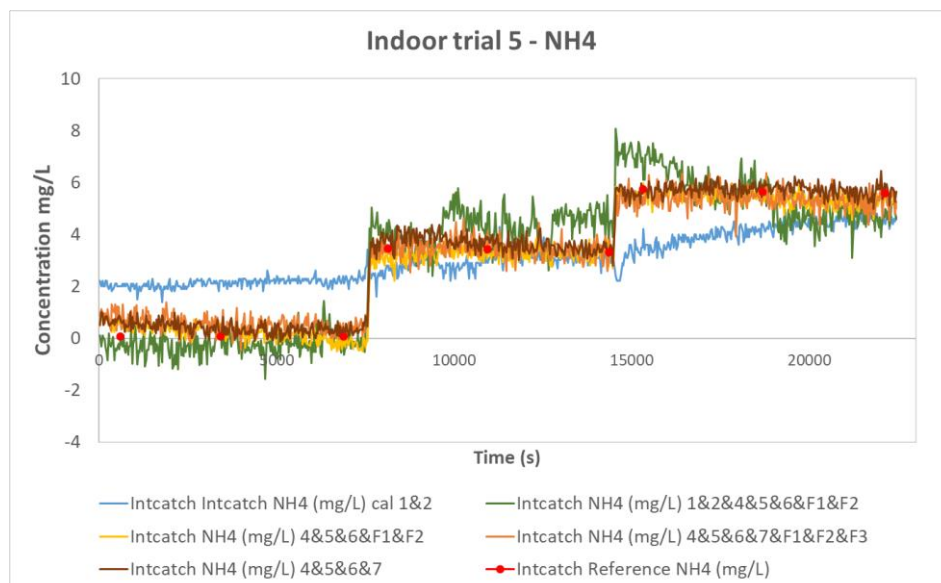


Figure 45: Ammonia Measurement of indoor trial 5 with five different calibrations and the reference point of the laboratory measurement

While the BOD₅ and ammonia is increasing with contamination raise, the pH is decreasing seen in Figure 46

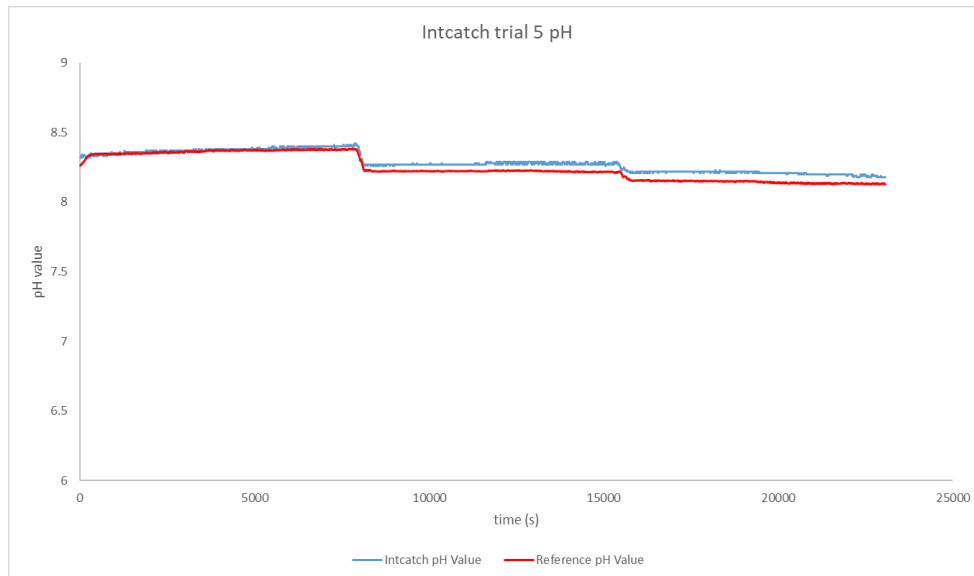


Figure 46: pH-measurement of indoor trial 5 with the reference measurement as a red line

Also, the amount of oxygen in the water is decreasing with increasing pollution stated in Figure 47.

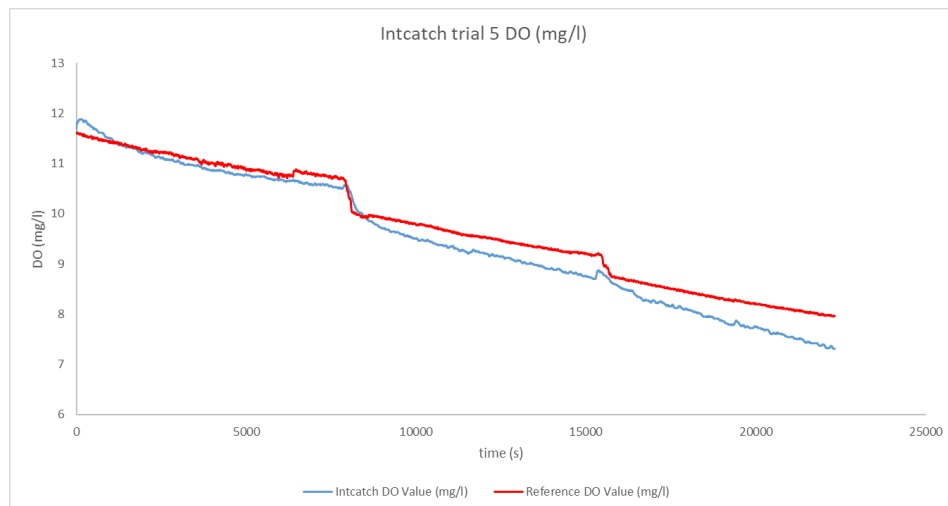


Figure 47: Dissolved Oxygen measurement of indoor trial 5 with the reference measurement as a red line

Curriculum Vitae

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Greek	A2	A2	A2	A1	A1

(*) Reference Level of the Common European Framework of Reference for Languages

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tennis
bowling
billiards
biking

Affirmation

I certify that the master thesis was written by me, not using sources and tools other than quoted and without the use of any other illegitimate support.

Furthermore, I confirm that I have not submitted this master thesis either nationally or internationally in any form.

Vienna, 05.05.2020, Dominik Rapberger