Professur für Hydrologie
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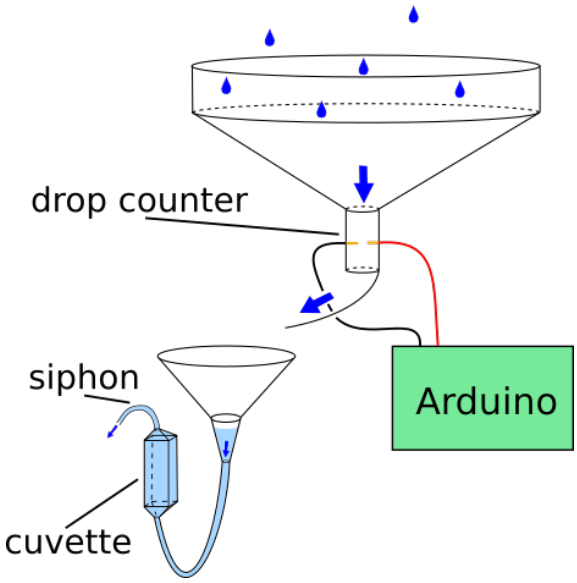
Niklas Tönsing

Linking Drop Counter to in-situ DOC measurements for studying forest hydrology



Master's thesis supervised by Prof. Dr. Markus Weiler
Freiburg i. Br., October 2021

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First Referee: **Prof. Dr. Markus Weiler**

Second Referee: **Prof. Dr. Friederike Lang**

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Abstract

The dynamics of carbon in the forest soil play a key role for global carbon storage, water quality, forest ecology and soil formation processes (Lukac and Godbold, 2011). Further investigation is required to fill research gaps on the carbon fluxes especially in the upper layers of the forest soil, the correlation of precipitation amount and carbon fluxes and the relevance of short timescale processes (Lee et al., 2015; Michalzik et al., 2001; Ruhala and Zarnetske, 2017). The aim of this work is to design a system that can be used in the forest O horizon to measure the flow rate of soil solution and the concentration of dissolved organic carbon (DOC). The functionality and limitations of the system are evaluated and its applicability to do the required investigation in the forest soil. It is tested additionally to what extent the results depend on place and time.
A drop counter is used to measure the flow rate. Its measurement accuracy is evaluated with applied precipitation of different intensity. Assuming that the DOC concentration correlates with the fluorescence intensity of the soil solution, the concentration is determined by excitating the solution with an 375nm LED and measuring the emission spectrum with a micro spectrometer. The spectroscopic DOC measurement technique is calibrated using artificial soil solutions with different DOC concentrations. Finally the performance of the combined system is tested in real case simulations.
The designed measurement system shows a successful operation in the real case simulation. Furthermore the measurement range and the accuracy of the measured quantities are appropriate for the intended purpose of in-situ measuring in the forest soil. However, the experiments show that the correlation between DOC concentration and fluorescence intensity does depend on place and the dependency on time can not be excluded completely. In conclusion the system is ready for field operation, merely minor adaptions have to be done beforehand. As the mentioned correlation depends on place the calibration of the DOC measurement must be done for each new site individually and as it might depend on time in the beginning the concentration should be cross-checked by analysing solution samples in the laboratory.

Zusammenfassung

Die Dynamik von Kohlenstoff im Waldboden spielt eine entscheidende Rolle im Zusammenhang mit globaler Kohlenstoff-Speicherung, Wasserqualität, Waldökologie und Bodenbildungsprozessen (Lukac and Godbold, 2011). Weiterer Forschungsbedarf besteht zur Analyse des Kohlenstoffstroms, insbesondere in den oberen Schichten des Waldbodens, der Korrelation zwischen Niederschlagsmenge und Kohlenstoffströmen sowie der Bedeutung von Prozessen kurzer Zeitskala (Lee et al., 2015; Michalzik et al., 2001; Ruhala and Zarnetske, 2017). Ziel dieser Arbeit ist es ein System zu entwickeln, welches ermöglicht zeitgleich den Sickerfluss der Bodenlösung als auch die Konzentration des darin gelösten organischen Kohlenstoffs (DOC) im O Horizont des Waldbodens zu messen. Die Funktionalität und die Begrenzung des Messsystems und die Anwendbarkeit zur Untersuchung aktueller Forschungsfragen werden evaluiert. Außerdem wird untersucht inwieweit die Ergebnisse von Ort und Zeit des Messvorgangs abhängen.
Zur Messung des Sickerflusses wird ein drop counter genutzt, welcher Tropfen gleichen Volumens zählt. Durch Beregnungsversuche mit unterschiedlichen Intensitäten wird seine Messgenauigkeit analysiert. Unter der Annahme, dass die DOC Konzentration mit der Fluoreszenzintensität einer Bodenlösung korreliert, wird die DOC Konzentration bestimmt indem die Bodenlösung durch eine LED mit einer Wellenlänge von 375nm angeregt und dann mit einem Mikrospektrometer das Emissionsspektrum gemessen wird. Die Messung der DOC Konzentration mit dem Spektrometer wird unter Verwendung künstlicher Bodenlösungen unterschiedlicher Konzentrationen kalibriert. Schließlich wird das zusammengesetzte Messsystem in realitätsnahen Simulationen getestet.
Das entwickelte Messsystem zeigt in den Simulationen das erwünschte Verhalten. Außerdem sind der Messbereich und die Messgenauigkeit geeignet, um vorgesehene in-situ Messungen im Waldboden durchzuführen. Allerdings wird festgestellt, dass die Korrelation zwischen der DOC Konzentration und der Fluoreszenzintensität vom Standort abhängt und eine zeitliche Abhängigkeit nicht vollständig ausgeschlossen werden kann. Schlussfolgernd kann gesagt werden, dass das Messsystem nach Fertigstellung kleinerer Anpassungen bereit für den Einsatz im Feld ist. Da die erwähnte Korrelation ortsabhängig ist, muss die Kalibrierung der DOC Messung für jeden Standort separat durchgeführt werden. Die in-situ Messung sollte zu Beginn im Labor durch Stichproben gegengeprüft werden, da eine Veränderung mit der Zeit nicht ausgeschlossen werden kann.

1 Introduction

Forests are one of the most widespread and important terrestrial ecosystems. They cover about 31% of the world's land surface (FAO and UNEP, 2020). Therefore they play an important role in many global biogeochemical cycles interchanging compounds with the atmosphere and the hydrosphere(Lukac and Godbold, 2011). In this thesis we will take a closer look at the carbon cycle and zoom in on the forest floor, the topmost part of the forest soil. The soil itself plays a special role in these cycles because it's placed between the atmosphere and the lithosphere, and it belongs to the hydro - and biosphere (Lukac and Godbold, 2011).

1.1 Global Carbon Cycle and Climate Change

Forest soils store carbon under certain conditions, therefore it is important to study the role of forests in the global carbon cycle (GCC), especially in consideration of ongoing climate change (Lukac and Godbold, 2011). The carbon (C) stored in global soils is considered to be as much as three times the carbon stored in all plants, and carbon in soils and plants put together store as much as three times the carbon in the atmosphere, but C stored in soils is only about 0.02% of the inorganic C stored in carbonate rocks. Thus changes in C in soils and rocks can have a big impact on C in the atmosphere (Lukac and Godbold, 2011).

1.2 Soil Organic Matter

1.2.1 Origin and Dynamics

"Except from thermo-bacteria, all global biomass is produced by photosynthesis. Carbon enters the biosphere as CO_2 through photosynthesis and then goes through diverse ways until returning to the atmosphere in form of CO_2" (Lukac and Godbold, 2011, p.94). The time the carbon remains in the biosphere until it returns to the atmosphere varies from only seconds to millennia (Lukac and Godbold, 2011). There are two pathways for the soil organic matter (SOM) to enter the soil. The first is the decomposition of litter by microorganisms that falls on the ground, referred to as aboveground carbon allocation. The second is the carbon flux that comes from within the trees to support the root system and the mycorrhiza, referred to as belowground carbon allocation. The proportion of these two fractions can differ a lot but is usually of the same order (Lukac and Godbold, 2011). Inside the soil the

SOM can pass through three types of transformation: mineralisation, humification or assimilation by microorganisms (Lukac and Godbold, 2011).

1.2.2 Composition

"Soil organic matter consists of all of the carbon- containing substances in the soil, except inorganic carbonates. It is a mixture of plant and animal residues in various stages of decomposition, the bodies of living and dead microorganisms, and substances synthesized from breakdown products of all of these" (Binkley and Fisher, 2013, p.39). SOM appears in solid, colloidal, and soluble forms throughout the whole soil, distinguishable in the O horizon at the top of the soil but also in smaller proportions in the mineral horizons (Binkley and Fisher, 2013).

The inherited fraction of SOM originates directly from plant or animal litter and is not formed in the soil by decomposition. The bigger humified fraction is composed of complex aromatic compounds, which tend to be acidic. They are classified into humic acids, fulvic acids and humin (Lukac and Godbold, 2011). This classification defines the compounds by their solubility in acids. The humic acid fraction is soluble only in acids with pH < 2. The fulvic acid fraction is soluble in weak and strong acids and the humin fraction is not soluble in acids (Binkley and Fisher, 2013).

1.2.3 Ecologic Importance

The SOM plays an important role for most processes in the soil (Binkley and Fisher, 2013). It is the energy source for all the life inside the soil (Lukac and Godbold, 2011). The soil flora and fauna consuming SOM are important for nutrient cycling, maintenance of soil porosity and soil detoxification processes amongst other processes (Binkley and Fisher, 2013). As well as providing a source of nutrients for life in the soil, the SOM itself fulfils similar important functions, such as providing soil structure, bulk density, hydraulic conductivity, ion exchange capacity, water holding capacity and more. (Binkley and Fisher, 2013; Lukac and Godbold, 2011). Studies show that nitrogen, one of the most important nutrients in soil, is closely linked to the SOM (Binkley and Fisher, 2013). In addition, the water quality in water bodies depends on their carbon concentration and the water that comes from forested catchments is rich in carbon (Cory et al., 2011). Finally, as mentioned above, carbon can be stored in some forms of SOM for a long time, and thus be a sink for atmospheric carbon, mitigating the climate warming (Binkley and Fisher, 2013).

1.3 Organic Horizon

The Organic horizon (O horizon) is sometimes referred to as humus or as the forest floor, but these terms are confusing, because the term humus is used for a part of the SOM while the term forest floor suggests that the O horizon is not part of the soil. Therefore, the term O horizon will be used in this thesis. The O horizon is

most of the time a distinctive horizon of the forest soil. It may contain 20% or more of the total C in the soil (Binkley and Fisher, 2013). By definition, the O horizon is the top layer of a forest soil and ends where the proportion of mineral material prevails over that of organic material (often defined as $< 20\%$ or 30% organic matter by weight). The organic material in the O horizon consists of fresh plant and animal litter, partially decomposed litter and humic materials that arise as a byproduct of decomposition. Apart from soils with high physical mixing, the concentration of mineral material is low in O horizons.
As the microflora and fauna living in the soil use the litter in the O horizon as well as partly decomposed matter as food, most of the carbon returns to the atmosphere in the form of carbon dioxide, while a smaller part is humified into stable long-lasting compounds. Apart from carbon, other substances are also released as the litter decomposes, such as nitrogen, phosphorus and sulfur, which serve as nutrients for plants. (Binkley and Fisher, 2013).

1.3.1 O Horizon Categories

The O horizons appearing on Earth can be categorised as mor, mull and moder. Mull is usually found below deciduous trees. It is characterised by a thin ($0 - 5$cm) litter lay and a thick ($20 - 50$cm) A horizon that is well aggregated, porous and dark (Lukac and Godbold, 2011). Mor is usually found below coniferous forests. It shows a slower decomposition, with a thicker ($10 - 20$cm) litter layer which shows a sharp division to the mineral horizon. The A horizon below is typically pale or white, compact and poorly drained (Lukac and Godbold, 2011).

1.3.2 O Horizon Division

The horizon is usually divided into three layers (Lukac and Godbold, 2011):

- Litter (L) layer: undecomposed litter with identifiable origin
- Formultning/fragmentation or fermentation (F) layer: material that is partly decomposed, some of it can still be identified
- Humus (H) layer: consists of completely decomposed matter, with unidentifiable origin

1.4 Soil Water

Soil particles and chemical compounds are dissolved and transported in soil water. It thus allows stratification of soil horizons. Furthermore, microorganisms that live in the soil can only acquire resources through their cell walls by osmosis, and thus need organic matter that is dissolved in water for their nutrition. They release enzymes

into the soil water that break the compounds into smaller molecules. Finally, the water in the soil also affects soil temperature and aeration (Binkley and Fisher, 2013; Lukac and Godbold, 2011).

1.5 Soil Forming Processes

The soil forming process is always connected to the movement and transformation of particles in the soil. Podzolisation is a classic example. Chemical and physical eluviation and illuviation lead to a bleached eluvial horizon and an enriched illuvial one just below it (Lukac and Godbold, 2011, p. 7f).

1.6 Dissolved Organic Matter

Dissolved Organic Matter (DOM) is usually defined as the fraction of organic matter in solution that passes through a filter (typically 0.45µm or 0.7µm) for practical purposes, due to the difficulty to distinguish dissolved from suspended matter (Bolan et al., 2011; Cory et al., 2011). It is only a small fraction of the total SOM (Binkley and Fisher, 2013). The portion of carbon in DOM by weight is between 45 and 50%. Thus DOM can be determined by measuring the dissolved organic carbon (DOC) and multiplying by a factor of around 2. Often the terms DOM and DOC are used interchangeably (Binkley and Fisher, 2013; Cory et al., 2011). DOM is a complex mix of different organic compounds like amino, fatty and nucleic acids, carbohydrates, polyphenols and organic acids. By molar quantity the concentration of DOC is often similar to that of inorganic ions (Binkley and Fisher, 2013). By mass the concentration of DOC in solutions of the O horizon is usually between 20 and 90 $mgCl^{-1}$ (Michalzik et al., 2001).
DOC is one of the three forms in which carbon is transported in water. The two others are dissolved inorganic carbon, like dissolved carbon dioxide, bicarbonate and carbonate ions, and particulate organic matter (POM). The DOC that reaches water bodies is a food source for life in aquatic ecosystems (Cory et al., 2011).
Different studies show, that between 10 % and 20 % of the original litter mass enters the A horizon in the form of DOM. In one study in North Carolina, 14% percolated into the A horizon as DOM, only 2% entered the A horizon as physical fragments and 5% remained in the O horizon. The rest returned to the atmosphere in form of CO_2 (Binkley and Fisher, 2013). Another study shows, that the DOC and DON fluxes from the O horizon correlate with annual precipitation. However, there is still a lack of knowledge about the dynamics inside the O horizon (i.e. from the L layer to the F layer), and up until now, most of the data about the dynamics of DOM in forest soils is generated in laboratory experiments (Michalzik et al., 2001).
Chromophoric or Colored Dissolvesd organic matter (CDOM) absorbs visible and ultraviolet light, and has the effect of protecting aquatic ecosystem from harmful radiation. Furthermore the DOC plays an important role for the mobilisation of

trace metals and contaminants (Cory et al., 2011).

1.7 Measurement of Dissolved Organic Matter

"We generally measure soil organic matter by a one-time determination of soil organic carbon, but this is akin to determining a person's wealth by looking at his assets and disregarding his liabilities." (Binkley and Fisher, 2013, p. 39) Figure 1.1 shows the DOC concentration in a river over time with different sampling frequencies. It visualises that crucial information about the dynamics might be missed when using a too low sampling frequency (Jollymore et al., 2012). As mentioned before, DOM can be determined by measuring DOC, because DOM is roughly 50% carbon by mass. In the laboratory this is commonly done by high temperature combustion or wet oxidation methods (Cory et al., 2011).

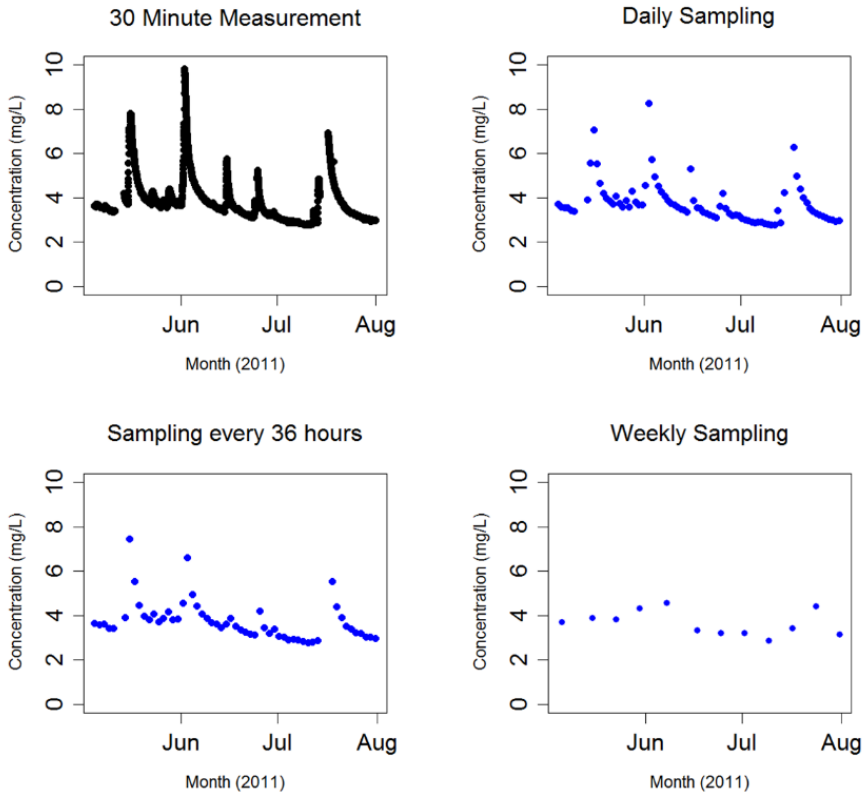

Figure 1.1: Exemplarily the DOC concentration in a river over time with different sampling frequencies is shown. For the low frequencies important properties of the dynamic are missed (Jollymore et al., 2012).

1.8 DOM Measurement by Absorbance and Fluorescence Spectroscopy

Another possibility to measure DOM concentration which can also be used in-situ is the spectroscopic measuring. There are two different types of spectroscopy used: Absorbance and fluorescence spectroscopy. With Absorbance spectrometers, the concentration of chromophoric fraction of DOM (CDOM) can be detected, and with fluorescence spectrometers, the concentrations of fluorescent DOM (FDOM). This concentration can be used to determine the total DOM concentration (Ruhala and Zarnetske, 2017).

1.8.1 Absorbance Spectroscopy

In general the UV-VIS absorbance of CDOM correlates highly with DOC concentration (i.e. $r^2 > 0.95$) (Ruhala and Zarnetske, 2017). But the absorbance drops with rising emission wavelength and also depends on the quality and quantity of CDOM in the sample, because CDOM contains the fulvic and humic acid fractions and can additionally contain nonhumic and potentially more labile fractions (Cory et al., 2011). The most common approach identifying DOC quality and quantity is finding the specific UV absorbance (SUVA). It is "defined as the decadic UV absorbance coefficient at 254 nm in inverse meters (m^{-1}) divided by the DOC concentration measured in $mgCl^{-1}$" (Cory et al., 2011, p. 123) and it positively correlates to the aromatic carbon content of the fulvic fraction of DOM (Cory et al., 2011).

1.8.2 Fluorescence Spectroscopy

Fluorescent DOM (FDOM) is the part of DOM that fluoresces at certain excitation light (Ruhala and Zarnetske, 2017). Fluorescence spectroscopy is considered to be more sensitive compared to absorption spectroscopy. However, different fractions of the DOM have different fluorescence behaviour, and their concentration may or may not correlate with the bulk DOC concentration. Therefore it is important to always carefully check the relation between the fluorescence signal and the DOC concentration for each site. Typically spectroscopy is used to find the concentration of one known substance. In the case of DOM we have a group of many different molecules, the composition of which we don't know. This makes it difficult to analyse the fluorescence spectra of a solution with DOC. Particulate organic matter (POM) also contributes to the fluorescence signal and can distort the measurement of DOM if not filtered out. It is still unclear which parts of DOM contribute to fluorescence signals, and more research should be done to answer that question. As the fluorescent part of the DOM must be aromatic compounds at least an upper limit of fluorescent carbon of 12-30% can be deduced. Even if the amount of fluorescent carbon is supposed to be only 1% of the bulk DOC, it is considered to be a good proxy as it behaves similarly to other non-fluorescent parts. Studies demonstrate

that fluorescence signals from terrestrial-humic carbon correlate better with bulk DOC concentrations than signals from amino acids. Furthermore, they show that the fluorescent signal varies with space and time between and among systems, which indicates that the amount of fluorescence per carbon differs among systems (Cory et al., 2011).

1.8.3 Development of in-situ Spectroscopy

At first in-situ spectroscopy was used to study the DOC dynamics in marine and coastal environments, as well as in water treatment and management, and is recently used in rivers, too. In-Situ FDOM fluorometers typically use an LED with a single wavelength for excitation and measure the emission at a single wavelength. They are used to study seasonal, event and diurnal variations in DOC quantity and quality. This helps to understand the annual DOC flux, as a large portion occurs during short storm events, and the connection between short and long timescale observations. The spectrometers used in the literature are usually commercial solutions that already provide a light source and a control system like the s::can, spectro::lyser and therefore have a high cost. To improve in-situ methods, they should be coupled with discrete DOC sampling for direct calibration (Ruhala and Zarnetske, 2017).

1.8.4 In-situ Spectroscopy in Forest Ecosystems

So far in-situ spectroscopy for DOC measurement has only been used in aquatic systems with forested basins, but not in the forest soil itself (Cory et al., 2011). Those studies indicate, that the DOC load from the forest is linked to the discharge from the forest (Lee et al., 2015). As stated in section 1.6 the laboratory studies also show that the DOC load correlates with the precipitation in the forest, but there is still a lack of data especially for the upper layers of the O horizon (Michalzik et al., 2001). Therefore in-situ spectroscopy within the forest soil could help to give more insight about the dynamics of DOC in the forest soil. It might help to answer open questions, like how the DOC flux is linked to other soil processes, how much DOC reaches the A horizon or leaches to surface waters or if the concentrations are diluted for high rainfall intensities (Michalzik et al., 2001). In this study new possibilities to achieve these goals are investigated.

2 Object of Research

The main question that guided me through the project work of my master's thesis is:

- **Is it possible to measure the flow rate of water and its DOC concentration in-situ in the forest floor using a low budget setup with a drop counter and a micro spectrometer?**

In order to investigate the research question the following hypotheses are proposed:

1. The measurement range of the drop counter does cover the common flow rates of solution through forest soil.
2. The measurement range of the spectrometric unit does cover the common concentrations of DOC in soil solutions.

Furthermore two sub questions are formulated to evaluate the quality of the results:

1. How accurate is the measurement with the setup and what are its limits?
2. How much do the results and its quality depend on place and time?

3 Methods

3.1 Experimental Setup

The substantial parts of the main experimental setup are drafted in figure 3.1 and figure 3.2. The topmost part is a drop counter from the ATMOS 41 Weather Station from METER Group. Its funnel collects the water or other liquid that falls on its surface and guides it to a flared hole where drops of a known size are formed. These drops fall past two gold pins that are connected to a voltage. When a drop falls by, the circuit is closed, and the drop is detected by the change in voltage. Below the drop counter is another funnel that guides the liquid to a hose. The liquid then flows through a cuvette and leaves the system through a siphon.
Figure 3.2 shows the spectroscopic unit that is connected to the cuvette. It consists of an LED with a peak wavelength of 375nm, a spectrometer that is placed in a right angle to the LED to capture the fluorescence from the sample. Both devices are connected to an Arduino micro controller to operate them and read the data, which is then saved on an SD-Card.

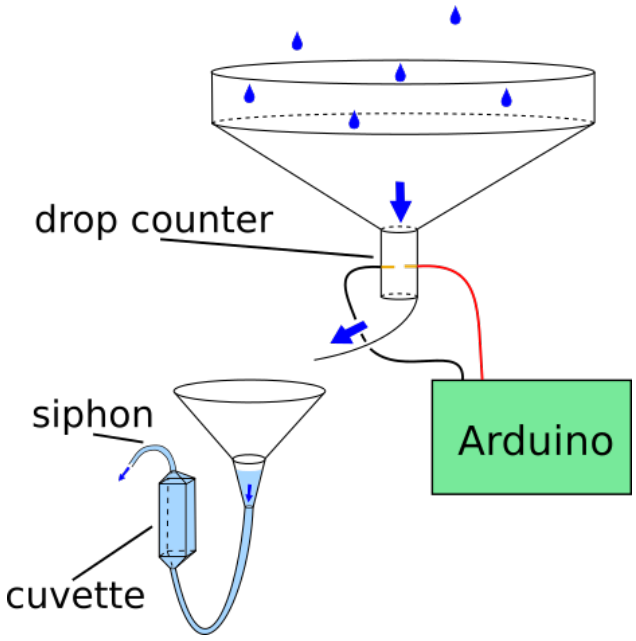

Figure 3.1: The final experimental setup that is used for continuous measuring. The spectrometer, LED and SD-Card are shown seperately in figure 3.2.

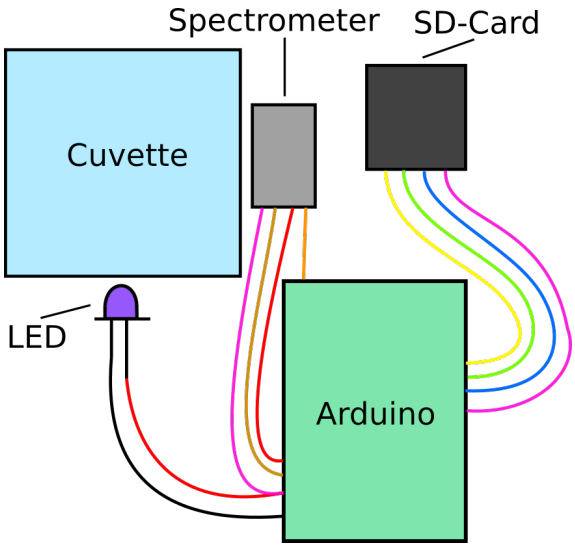

Figure 3.2: Topview of the spectroscopic unit with LED and spectrometer in right angle and all devices connected to teh micro controller. In the experiment the cuvette, the spectrometer and the LED are covered by a black box.

3.1.1 Drop Counter

The flow rate of water in the soil can be measured by a drop counter. Figure 3.3 shows a cut through the drop counter. The aperture has a surface of 68.08 cm^2. The spring above the hole holds back bigger particles. At the flared hole drops with a volume of 0.116 ml are formed. This can change for high or low intensities. According to the manual, the drop counter can measure precipitation intensities between 0 and 400mm/h, with a resolution of 0.017mm and a precision of $\pm 5\%$ for intensities between 0 and 50mm/h (Meter Group AG, 2020).
Figure 3.4 shows the 3.5-mm stereo plug to connect the drop counter to a data logger. The power side is connected to one of the two pins and the digital communication side to the other one. The drop counter needs an input voltage on power between 2.8 V and 5.5 V (Meter Group AG, 2020). Therefore power is connected to the 5 V pin of the Arduino and the digital communication is connected to an analogue Pin of the Arduino. In addition, the analogue pin is connected to ground via a resistance of 22 kΩ. The Arduino reads the voltage on the Digital communication pin all the time and returns integers between 0 and 1023 correlated to the voltage. When there is no drop, it is between 0 and 200. When a drop falls through it jumps on a value above 900 and then falls down in some microseconds. It always falls below a value of 700 before the next drop. Thus when the analogue value rises above 700 and falls below 700 afterwards that is counted as one drop.

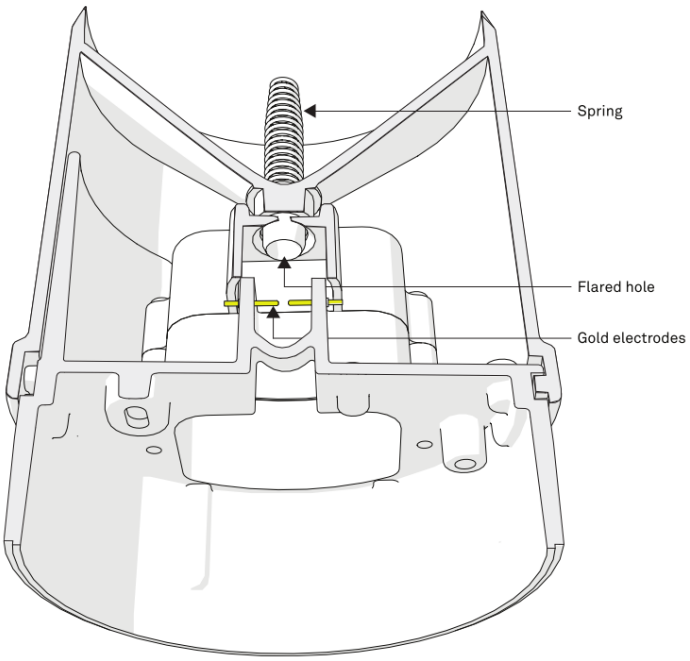

Figure 3.3: Cut through the Atmos drop counter with indications of teh relevant parts (Meter Group AG, 2020).

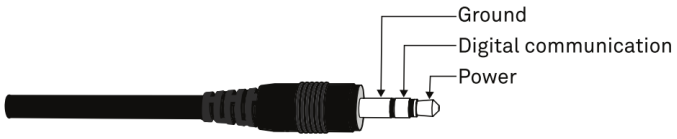

Figure 3.4: 3.5mm stereo plug connector of the drop counter and its wiring (Meter Group AG, 2020).

3.1.2 Siphon

A siphon takes advantage of the principle of the communicating vessels. The siphon used in this setup has two water levels: A high threshold level and a low emptying level. When the cuvette system is not filled the water level in the funnel has to exceed the threshold level to overshoot the highest point of the siphon. Then the liquid flows through until the low level is reached. The funnel and the siphon are placed so that the low level of the siphon is exactly where the funnel becomes smaller, so that no air enters the cuvette while in process.

3.1.3 Spectrometer

Fractions of the DOM have absorbance and fluorescenece behaviour, namely the CDOM and FDOM. Therefore a spectrometer can be used to measure DOM in a solution. The spectrometer used for this project is a Hamamatsu C12880MA, a micro spectrometer with high sensitivity. Figure 3.5 shows a picture of the spectrometer on a breakout board with LED and laser as used in the experiments.
Typically, the components of a spectrometer are an entrance slit, a collimating lens, a transmission grating or a prism to break up the spectrum, a focusing lens and an image sensor (see Fig. 3.6). The C12880MA has a reflective grating instead of the transmission grating and can therefore be built in a very compact form (see Fig. 3.7).
The spectrometer measures the spectrum between 311nm and 882nm with a spectral resolution of maximal 15 nm. The breakout board has 12 Pins which are connected to the Arduino. Ten Pins are for the spectrometer and one for the Laser and the LED each. There exists an example code to control the spectrometer with an Arduino made by groupgets (Pure Engineering LLC, 2016).
The absorbance of DOC decreases with increasing wavelength and the absorbance is typically measured between 250nm and 300nm. As the used spectrometer only measures at 311nm and above fluorescence spectroscopy is used to measure the DOC concentration. In (Lee et al., 2015) several studies that use an excitation wavelength of 370nm for fluorescence measurement are presented. Therefore an LED with 375nm peak wavelength is used for the excitation.

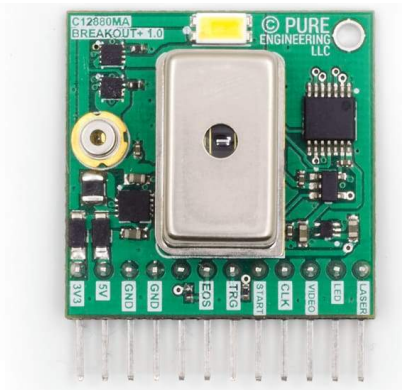

Figure 3.5: Hamamatsu C12880MA micro spectrometer with breakout board and indicated pins. Image Source: (Cool Components Ltd, 2021).

3.1.4 Micro Controller

All the electronic devices in the setup need a micro controller to send commands and receive observations. During the development of the setup an Arduino Uno was used. Later the whole system was changed to an Arduino Nano. Both Arduinos can

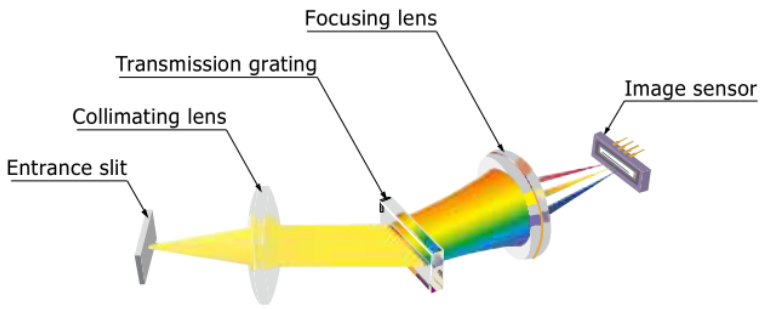

Figure 3.6: Illustration of the components of a classical spectrometer (Hamamatsu Photonics K.K., 2021).

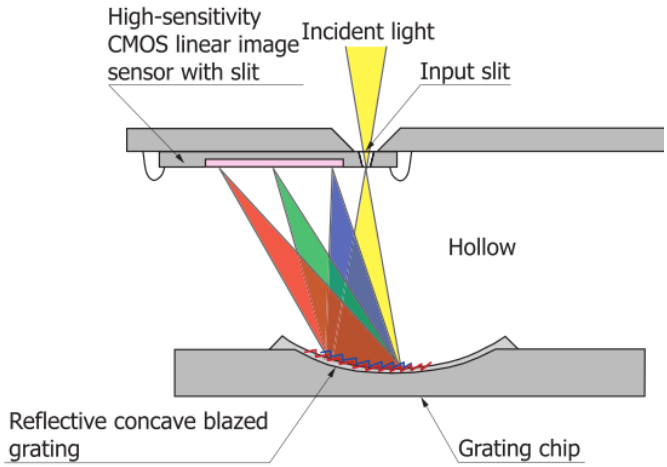

Figure 3.7: Illustration of the components of the C12880MA (Hamamatsu Photonics K.K, 2020).

be programmed using the Arduino IDE Software. The code is written on a PC and then uploaded to the Arduino via an USB cable. The USB port also provides the power for the Arduino and the connected devices. All used devices are controlled by the Arduino: the dropcounter, the LED, the spectrometer and the SD Card module.

3.1.5 SD Card Module

In order to save the data with a timestamp a data logging shield by Deek Robot is used. On the shield is a Real Time Clock (RTC), a coin cell for the RTC power supply and a micro-SD card slot. The module is connected to the Arduino. It communicates with the SD card over Serial Peripheral Interface (SPI) and with the RTC over Inter-Integrated Circuit (I^2C) (Draeger, 2017).

3.2 Calibration

The spectrometer does not measure a DOC concentration directly but a light intensity with values between 0 and 1023 and an arbitrary unit. Thus, to obtain the DOC concentration in the sample from these values the spectrometer needs to be calibrated. Therefore the spectra of samples with known DOC concentrations are taken and the functional relation between the spectral values and the concentration is determined.
The calibration process is performed as followed:

1. Take samples of forest floor
2. Create artificial soil solutions from samples
3. Dilute solution samples
4. Measure spectra of diluted samples
5. Measure total carbon concentration in non-diluted samples
6. Fit a regression function to calibration data

3.2.1 Soil Sampling

Samples from three forest sites in Freiburg are taken. Figure 3.8 shows the positions where the samples are taken. The sites are chosen to represent different geology and vegetation and thereby different soil conditions. On each position a bulk sample from the topmost 5 - 10 cm is taken with a shovel.

First Site

The first sample was taken on the Schönberg which forms part of the foothill zone of the Upper Rhine Plain. The position is located on a hill slope above a little stream. The predominant trees are beeches and firs. There is a lot of ground vegetation like ivy and others.

Second Site

The second sample was taken at the foot of the Brombergkopf which belongs to the Black Forest. The position is located on a small plateau between two slopes, close to a junction of dirt roads. The predominant trees are spruces, but there are also some beeches and other trees. There is not much ground vegetation, only some moss, blackberries and small spruces. The O horizon is very thin and deadwood is laying at the place.

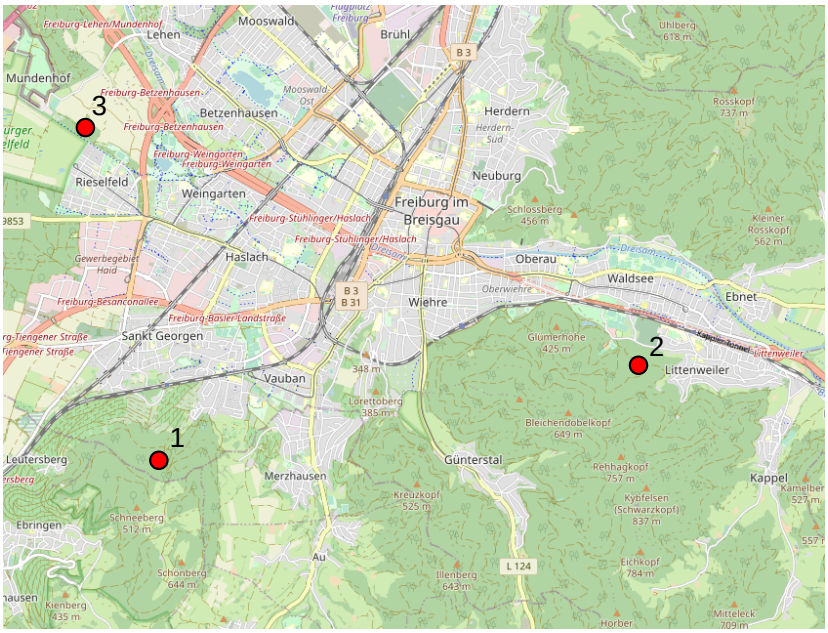

Figure 3.8: Map of Freiburg showing the soil sampling sites. Image source: osm.org

Figure 3.9: Picture of the forest where the first sample was taken. The trees on the top are beeches.

Third Site

The third sample was taken in the Landmattenwäldle, a small forest that lays in Upper Rhine Plain. It is composed by various deciduous trees, such as elms, acers

and ashes. There is a lot of ground vegetation like ivy, wood garlic and blackberries but little litter. It is difficult to distinguish the O horizon from the A horizon.

Figure 3.10: Picture of the forest where the second sample was taken. The trees in the picture are spruces.

Figure 3.11: Picture of the forest where the third sample was taken. It shows dead wood on the ground and diverse ground vegetation.

3.2.2 Creation of Serial Dilution

The aim of this procedure was to get an artificial soil solution with high concentration of DOC for each bulk sample and then dilute them on 6 concentrations for calibration purpose. In order to get a highly concentrated soil solution six tablespoons of each sample are mixed with 200ml of deionized water and placed on a shaker for 60 minutes (see Fig. 3.12).
Afterwards the mixtures are filtered several times with sieves, coffee filters and filter paper, going from coarse to fine. In the end there are three solutions that contain some CDOM apparently (see fig. 3.13).
In the last step every sample is diluted with deionized water with a fraction of the solution of 5, 10, 25, 50, 75 and 100%. A 4ml sample of each concentration are prepared in a test glass (see fig. 3.14).

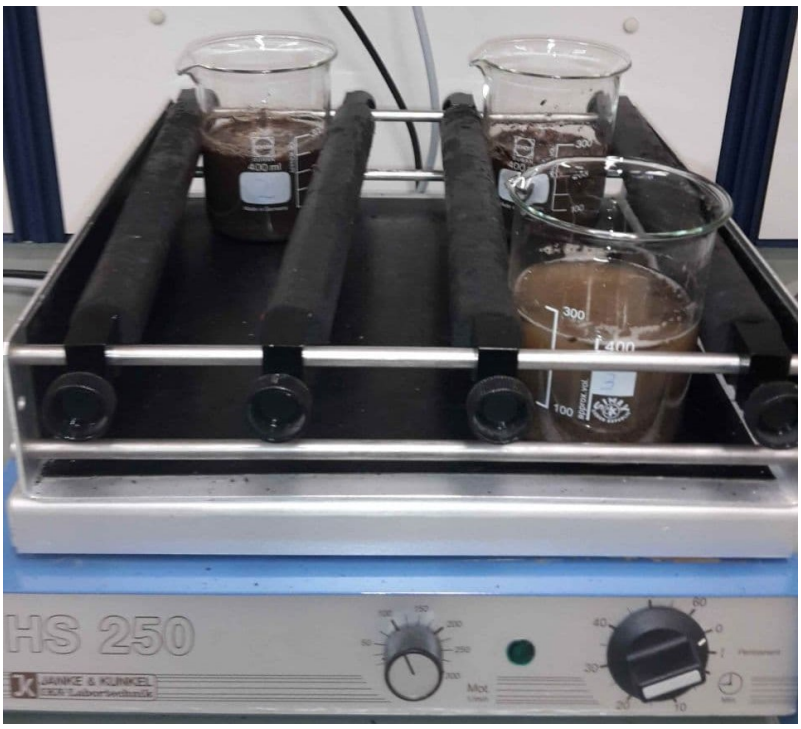

Figure 3.12: The mix of bulk sample and water was placed on the shaker for 60 min.

Figure 3.13: The artificial soil solutions from the three bulk samples show different colours, especially the one from the coniferous forest.

Figure 3.14: The serial dilution of sample 1 with 5, 10, 25, 50, 75 and 100% solution, that is used for the calibration.

3.2.3 Spectroscopic Measurements

For the spectroscopic measurement of the calibration solutions, a slightly different experimental setup is used. Figure 3.15 shows an image of the essential parts. There is no need of the drop counter nor the SD card module and instead of the flow-through cuvette a glass cuvette with a closed bottom is used. The cuvette has a volume of 3.5ml. For the measurement a sample volume of 3ml is filled in. For every sample the spectrum is measured 10 times with 4 different delay times each time (20, 50, 100 and 200ms).

3.2.4 Combustion Measurements

For the determination of the total amount of carbon in the solution samples a combustion measurment method is used. At the chair of soil ecology they have a TOC Analyser (Analytik Jena multi N/C 2100S) which uses high-temperature combustion at 950°C to oxidate all carbon in the sample and then measures the amount of produced carbon dioxide to determine the amount of carbon in the sample (Analytik Jena GmbH, 2020). The three samples are filtered with a 0.45µm membrane filter and both the filtered and unfiltered samples are analysed with the TOC Analyser.

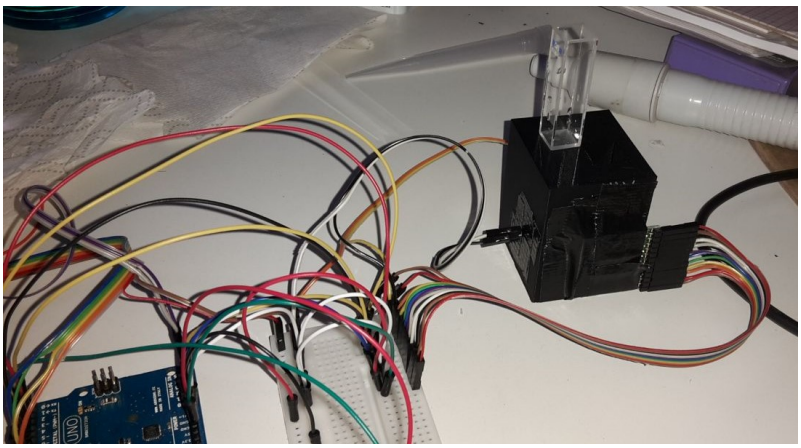

Figure 3.15: The black frame holds the glass cuvette, the spectrometer and the LED and shields stray light. The cables connect the spectrometer and the LED with the Arduino.

3.2.5 Calibration Regression

Noise Subtraction

For noise subtraction the spectrum without excitation light was measured and subtracted from every other spectrum (Resch-Genger et al., 2005).

Fluorescence Peak Integral

Every sample yields a spectrum between 311 and 758nm with intensities between 0 and 1023 in an arbitrary unit. Figure 3.16 exemplarily shows the fluorescence spectrum of sample 1 with a delay time of 50 milliseconds and different dilutions. Just like the example each spectrum exhibits the excitation peak around 375nm which is oversaturated and an emission peak around 480nm. The emission intensity depends on the sample concentration and on the delay time of the spectrometer. For all spectra the minimum between the excitation peak and the emission peak was between 432 and 445nm and the maximum of the emission peak was between 475 and 482nm. Therefore it was decided to use the fluorescence peak integral from 440 to 521nm (480nm in the middle with 40nm to each side) for calibration purpose.

Analysis of Integration Values

The graphical representation of the integral values of all spectra shows that there is a linear correlation between the integral value and the delay time (see figure 3.18). On the other hand the dependence of the integral value on the DOC concentration is only linear for small concentrations. Figure 3.17 shows all integral values for sample 2 plotted over the concentration in vol%. It is apparent that the integral values increase linearly for values from 5 to 25% for all delay times. However, for values above 25% the integral values grow less and for values above 75% even diminish.

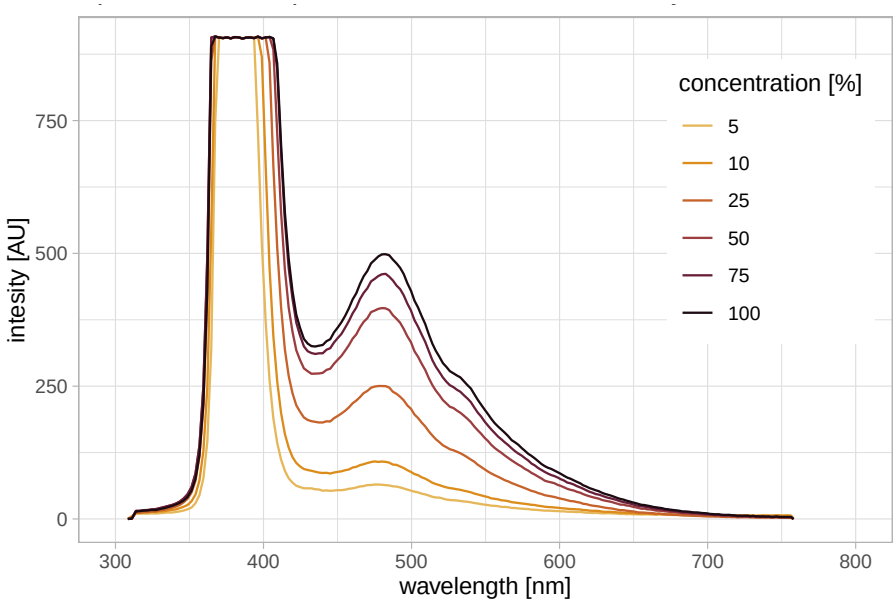

Figure 3.16: Spectrum of sample 1 with a delay time of 50ms and different dilution concentrations.

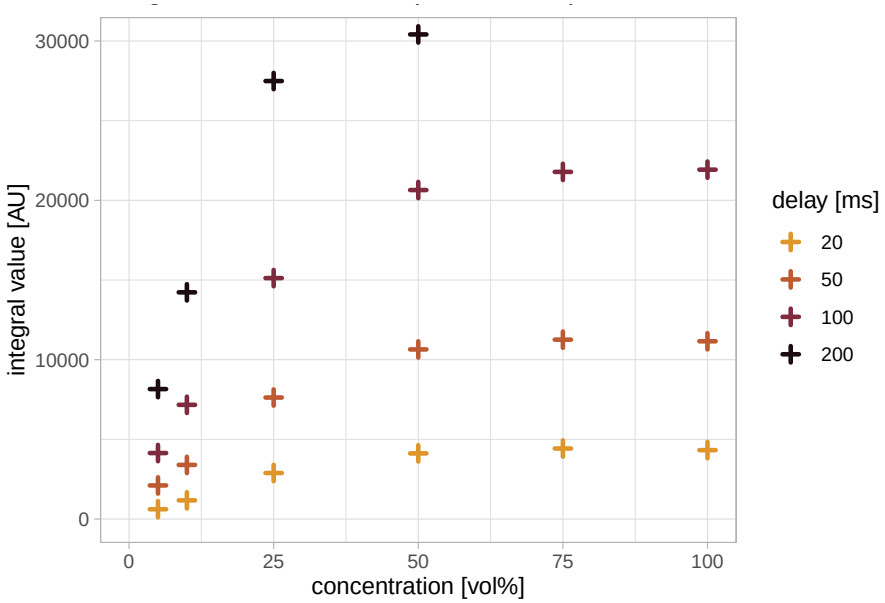

Figure 3.17: Integral values of all delay times plotted over the concentrations of sample 2.

Absorbance Correction

The reason for the attenuation of the integral values is the absorbance of light by chromophoric compounds in the sample, also called inner filter effect (Lakowicz, 2006). The fluorescence intensity, F, which correlates with the integral value de-

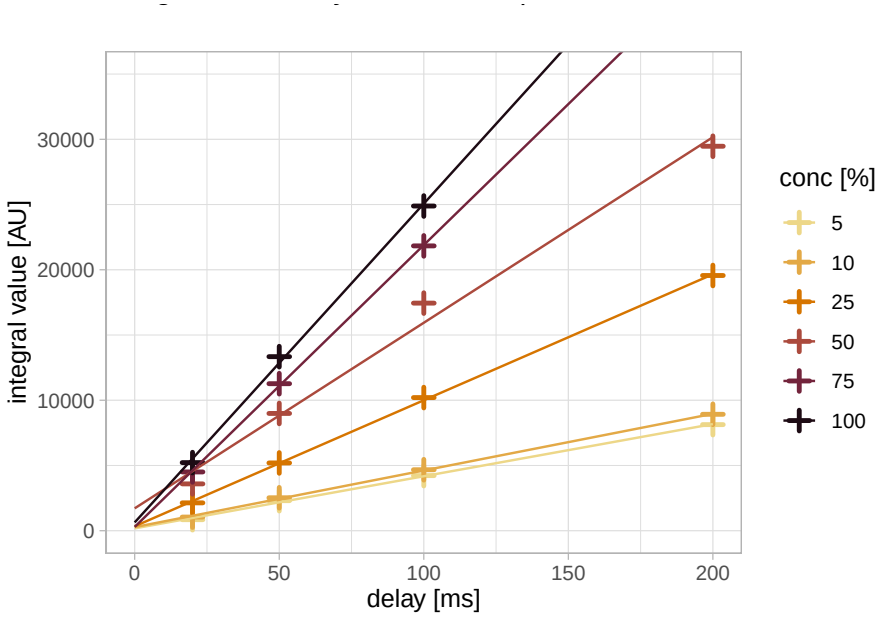

Figure 3.18: Integral values of all concentrations of sample 3 plotted over the delay together with linear regressions.

pends linearly on the DOC concentration, c and the incoming light I_0:

$$F = \beta \cdot \mathbf{c} \cdot I_0, \tag{3.1}$$

where β is any correlation factor. However, the excitation light as well as the emission light is reduced by absorbance on its way through the sample. The reduction through absorbance is described by the Beer-Lambert law that can be written in the following form (Lakowicz, 2006):

$$I_1 = I_0 \cdot \exp(-\alpha \cdot \mathbf{c}), \tag{3.2}$$

where I_0 is the incoming light, I_1 the outgoing light and α a correlation factor. Thus the fluorescence intensity under the influence of absorbance F_1 as a function of the concentration of the optical active substances can be written as:

$$F_1 = \beta \cdot \mathbf{c} \cdot \exp(-\alpha \cdot \mathbf{c}) \cdot I_0. \tag{3.3}$$

This function has the form $f(x) = x \cdot exp(x)$. The generic solution that solves this function in the way $y = W(y) \cdot \exp(W(y))$ is called the Lambert W function $W(x)$. As the corrected fluorescence decreases for high concentrations, the function $f(x)$ is not injective and thus the Lambert W function is a multivalued function with two

branches $W_0(x)$ and $W_{-1}(x)$ (Wikipedia, 2021). In this case $W_0(x)$ describes the interval where the fluorescence intensity grows with the concentration and $W_{-1}(x)$ the interval where the fluorescence intensity shrinks with the concentration. Hence, when using the function to calculate the concentration based on the fluorescence intensity one has to choose which branch of the Lambert W function to use. For practical purposes in the scope of this thesis the W_0 branch is used all the time.

Regression Curve

The aim of the calibration is to obtain a function that yields a DOC concentration for a known integral value X and a known delay time d. The inversion of equation (3.3) by use of the Lambert W function and the addition of the linear dependence on the delay time d results in a regression function with two variables and three parameters:

$$c_{\alpha,\beta,\gamma}(X,d) = \alpha \cdot W\left(\frac{\beta \cdot X}{d+\gamma}\right). \tag{3.4}$$

3.2.6 Absorbance Measurement

The absorbance measurement could be used for three purposes.

1. Measure the DOC concentration directly via absorbance spectroscopy (Li and Hur, 2017).

2. Use the measured absorbance to correct the inner filter effects of the fluorescence intensity (Lakowicz, 2006).

3. Use the absorbance value to determine the upper limit of the calibration function (3.4).

In order to measure the absorbance of the soil solutions the 3D printer was used to print another mount for the spectroscopic unit with two holes for LEDs. One hole is in right angle with the spectrometer for fluorescence spectroscopy and the second one is directly opposite of the spectrometer for absorbance spectroscopy. The same LED with the peak at 375nm that is used for fluorescence spectroscopy is used for the absorbance spectroscopy. The code that controls the measurement system was modified such that firstly the fluorescence LED is turned on and the spectrum measured and secondly the absorbance LED is turned on and the spectrum is measured and saved separately. The soil solutions from section 3.2.2 are used to test the absorbance setup.

3.2.7 Intensity Calibration

Intensity calibration refers to the part of the calibration process where the spectral data is normalised by comparing to a known reference. This is especially necessary when measurements from different spectrometers are compared or there are changes on the experimental setup. The literature proposes to use a standard reference material (i.e. Quinine Sulfate Dehydrate) with similar optical properties to DOC or take advantage of the Raman peak of pure water (Coble et al., 1993; Lawaetz and Stedmon, 2009; Velapoldi and Mielenz, 1980). For the calibration the fluorescence of the standard reference material or the water Raman peak is measured with the setup that is used for the concentration measurement. All data is then divided by the peak intensity of the reference material for normalisation (Lawaetz and Stedmon, 2009). For normalisation with Raman peak scattering the spectrum of deionized water is measured with different delay times (100, 200, 300, 500, 1000, 2000ms).
As the calibration with the artificial soil solutions yields good results and only one instrumental setup is used anyway, the calibration with a standard reference material is considered evitable.

Raman scattering

Additionally to the elastic Rayleigh scattering there also exist the less prominent inelastic scattering processes called Raman scattering. The spectrum of light scattered on a particle consists of the strong Rayleigh line with the same frequency as the incoming light as well as several side bands at lower and higher frequencies (Solé et al., 2005). The Raman scattering response to a certain light source is a fixed property of water and can therefore be used for calibration to compare different experimental settings. The peak wavelength of the Raman peak for water depends solely on the wavelength of the excitation light and can be calculated. For an excitation of 375nm the result is 427.3nm (Lawaetz and Stedmon, 2009).

3.3 Drop counter evaluation

This experiment is performed in order to check if and how accurate the flow rate of the soil solution can be measured with the drop counter. Metergroup designed a procedure to check the precipitation measurement of the Atmos 41 weather station, which equals the used drop counter (Meter Group AG, 2021). Following the instructions the subsequent steps were performed:

1. Balance the drop counter using a water level
2. Remove the metal spring from the funnel
3. Put a round filter in the funnel
4. Add 5 ml water per min to the funnel and measure during 6 minutes

Repeat the same procedure without filter and also with soil solution instead of water with and without filter. The volume measurement is also tested without filter, with soil solution and filter, with soil solution without filter and with 10ml water pro min. The samples are applied onto the drop counter using a pipette.

3.4 Flow-through Test

The aim of the following experiments is to check if the DOC concentration can be measured continuously, when solution flows through and if induced changes in concentration are detected Therefore several simulations of soil solution with changing DOC concentration are performed on the final experimental setup as described in section 3.1. The solutions are trickled on the drop counter using a pipette and the spectrum is measured every minute with two delay times (50 and 100ms). The first simulation is made with the solution 3 increasing the concentration from 0% over 10%, 25% to 50% and then decreasing back to 0%. The second and third simulation are done with solution 1 applying a 50% solution with an intensity of 5ml/min over 5 minutes. The fourth and fifth simulation are both done with a new solution (solution 1.1) prepared using the bulk sample 1 as described in section 3.2.2. In simulation 4 20ml of pure water is applied to the system for two minutes, then 20ml 50% soil solution is applied for two minutes and in the end 20ml of 10% dilution is applied for two minutes. In the last simulation pure water and a 50% solution are applied with an intensity of 10ml/min. The water is applied during two minutes and then the 50% solution is applied for 6 minutes.

3.5 Test with a Block of Forest Soil

3.5.1 Preparation

In the last step of the experiments for the master's thesis some tests with a piece of intact forest floor are done in the laboratory. For this purpose another sample is taken at the Schönberg. A place on the slope below Fesackerweg with big beech, oak fir and acer trees is chosen. There is plenty of space in between the trees and a lot of vegetation on the ground like blackberries and small trees. There is also a lot of deadwood and ants. The O horizon can be classified as mull type and the soil contains many roots.
With a spade a block of soil with a length of 30cm, a width of 20cm and a depth of 5-10cm is cut out of the ground. It is put in a plastic box of the same dimension (see Fig. 3.19). In one lower corner 3 holes of 2 mm diameter are drilled into the box, so that water can leave the box through these holes.

The idea is to put this box on an inclined plane and sprinkle the soil so that all the water that passes through the soil leaves the box through its holes. Therefor four feet are attached to a board so that the board is inclined to one corner when it stands on the feet. Besides a hole with a diameter of 8 cm is drilled into the board

Figure 3.19: A block of soil the size of the plastic box is cut with a spade and put into the box.

Figure 3.20: The box with the soil sample is placed on an inclined plane with holes in the low corner. Below the holes the measurement system of drop counter and spectrometer is positioned.

in the low corner, so that the water that drops out of the box can fall through that hole. The board with the box on top is then placed on the edge of a table so the water can drop past the table into the drop counter which is placed to collect the drops (see fig. 3.20).

3.5.2 Experimental Procedure

Several irrigation experiments are conducted using a spray bottle for irrigation of the soil. One shot of the bottle is about 1ml of water. Six irrigation experiments are done, two with 20 shots per minute, three with 60 shots per minute and one with 120 shots per minute. For each experiment an empty glass is weighed and placed below the outlet of the siphon. The spray bottle is filled with deionized water and also weighed. Then water is sprayed on the soil in the box with the respective intensity for a time between 5 and 20 minutes. Sometimes multiple glasses and fillings of the spray bottle are needed. The counted drops and measured spectra are saved on an SD card with a timestamp every 30 seconds and then transferred to a computer.
After the experiment the empty spray bottle and the full recipient are weighed again. The solutions from the recipient are bottled and its actual DOC concentration is

determined with the TOC analyser in the laboratory of the chair of soil ecology.

4 Results

4.1 Calibration

4.1.1 Combustion Measurement

The combustion measurement with the TOC analyser yields a DOC concentration for each of the three soil solution samples. The results are presented in table 4.1.

Table 4.1: The resulting DOC concentration from combustion measurement for the three samples, in parentheses the std. errors.

Sample number	DOC [mgC/l]
1	76.1(6)
2	99(1)
3	53.7(5)

4.1.2 Calibration Regression

To calibrate the integral values on the actual DOC concentrations the relative concentrations from the dilutions in % are multiplied by the absolute concentrations from table 4.1.
The result of the regressions on all calibration data is shown in figure 4.1. The regression curves using function (3.4) coincide well with most of the data points. Only a few points lay far away from the graph. It can also be seen, that the graphs have an upper limit around 100mgC/l. That is where the corrected fluorescence intensity and thus the integral value starts to decrease and so is described by the W_{-1} branch of the Lambert W function as written in section 3.2.5. The obtained fit parameters are presented in table 4.2.

4.1.3 Absorbance Measurement

The absorbance spectroscopy uses the effect, that the incoming light gets attenuated by the CDOM in the solution according to its concentration. In this case the absorbance is measured with different delay times and different incoming light intensity whereupon the measured intensity positively correlates with both. Figure

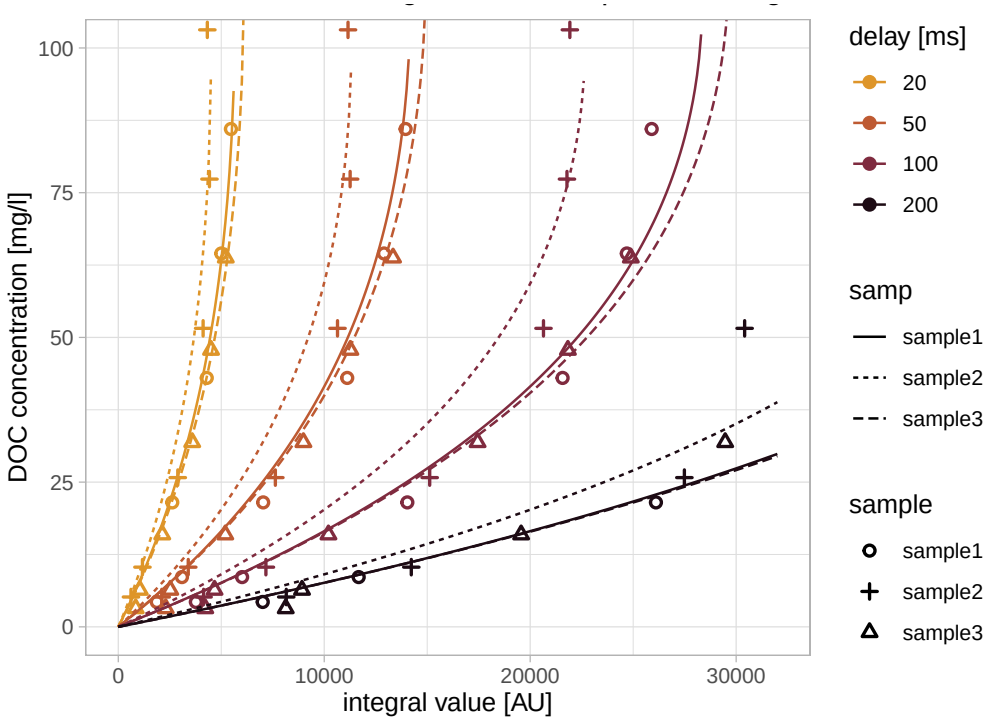

Figure 4.1: DOC concentrations of each dilution are plotted as points over the integral value of the corresponding spectrum. Additionally the graphical results of the non-linear regression are plotted as lines.

Table 4.2: The resulting parameters of the non-linear regression for the three samples, in parentheses the std. errors.

Sample number	α [mgl^{-1}]	β [ms^{-1}]	γ [ms]
1	-109(7)	$-1.30(3) \cdot 10^{-3}$	$1(50) \cdot 10^{-3}$
2	-100(12)	$-1.62(4) \cdot 10^{-3}$	-0.1(8)
3	-114(9)	$-1.25(5) \cdot 10^{-3}$	0.8(6)

4.2 shows the measured spectrum for a 100% dilution of sample 3 with the minimal delay time and the minimal incoming light intensity. Even with this setting the spectrometer gets oversaturated around 375nm. Therefore with this setup it is not possible to measure the absorbance of the solution. It would be necessary to further reduce the light intensity by using another light source, an intensity filter or a longer pathway through the sample. This would have gone beyond the scope of this thesis and could be investigated in another project.

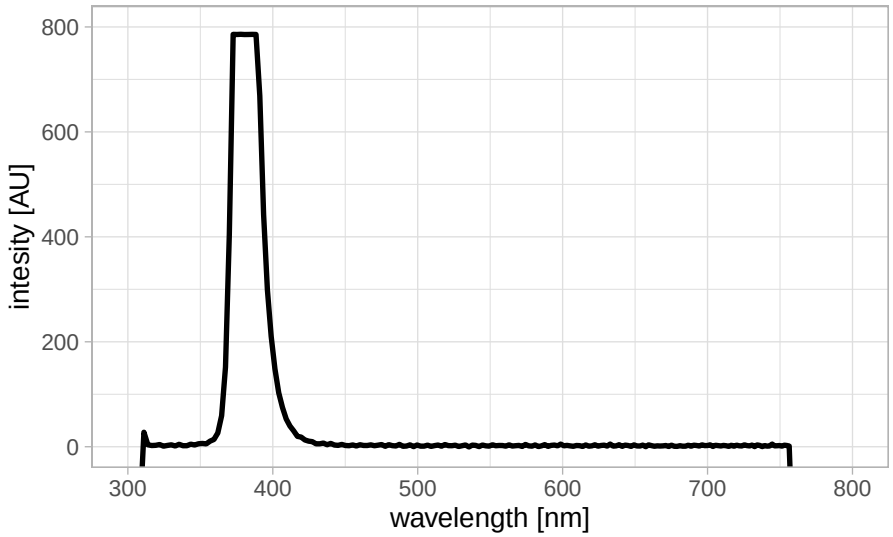

Figure 4.2: The Spectrum plot of a 100% dilution of sample 3 with the minimal delay time and the minimal incoming light intensity.

4.1.4 Intensity Calibration

The spectra of deionized water with different delay times are plotted in figure 4.3. For every delay time around the excitation peak of 375nm the image sensor gets oversaturated. For the delay times from 200ms above around 430nm a second peak is visible whose intensity increases with increasing delay time. This peak can be identified as the Raman scatter peak of the water itself.

4.2 Drop Counter Evaluation

Before using the drop counter the minimum and maximum intensity expected below a temperate forest floor is estimated. The low limit is 0mm/h, when now rain is falling and the high limit is deduced from the maximum rain intensities in Germany which is about 2mm/min equal to 120mm/h (Deutscher Wetterdienst, 2021). Considering the funnels surface of 68.08cm^2 this yields a maximum intensity of 14ml/min. As mentioned in 3.1.1 drops with a volume of 0.116 ml are formed at the drop counter. Therefore to calculate the volume the number of drops counted is multiplied by the volume of one drop. Before the procedure described in section 3.3 was done, the drop counter was already used to measure the volume in a test run. In that run 81ml solution was applied and the drop counter measured 34.8ml, which is only 43.0% of the applied volume. That is why the check of the drop counter was undertaken. The results are demonstrated in Table 4.3. The accuracy is the measured volume divided by the applied volume. The average accuracy is 88%.

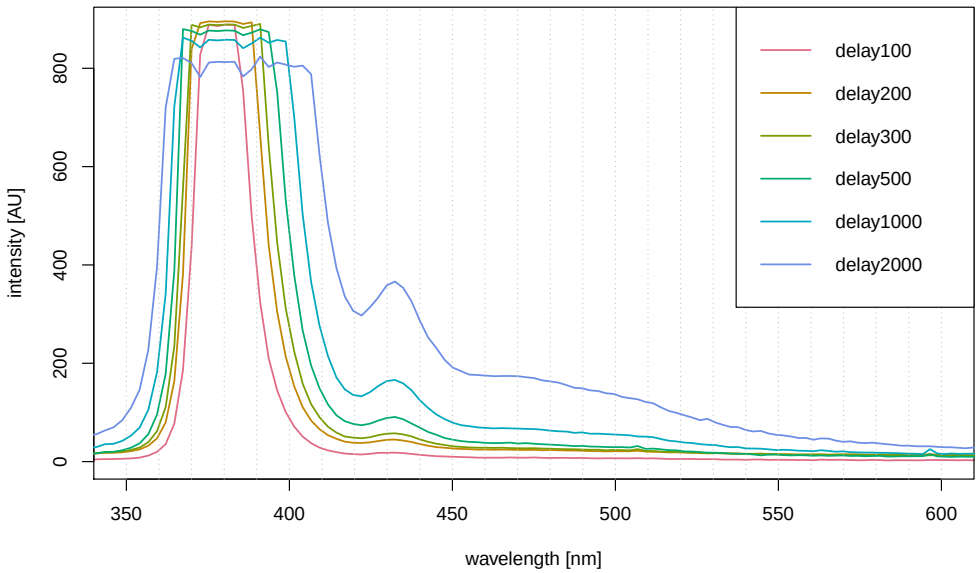

Figure 4.3: The Spectrum of deionized water with different delay times. For high delay times the Raman peak can be identified clearly.

Table 4.3: Comparison of applied and measured volume for different samples applied on the drop counter.

Sample	Filter	Intensity [ml/min]	Accuracy [%]
deionized water	yes	5	87
deionized water	no	5	88
soil solution 1	yes	5	96
soil solution 1	no	5	78
deionized water	no	10	84
soil solution 1	no	10	79
soil solution 1	no	10	107

4.3 Flow-through Test

For all the spectral data the mentioned fluorescence peak integral was taken. Then the calibration function (3.4) with the respective parameters was used to convert the integral values into DOC concentrations. These concentrations are plotted over time for the first, fourth and fifth simulation in figure 4.4 to 4.5. Simulations 2 and 3 do not reveal further information. In black the DOC concentration applied onto the drop counter is plotted. The values are obtained by multiplying the relative concentration (in %) with the total concentration (in mg/l) measured by the TOC-

Analyser. The total concentration of sample 1.1 was found to be 52.8(9)mg/l. Figure 4.6 shows that it takes about 4:30 minutes until the measured concentration reaches an equilibrium, which is equal to 45ml discharge.
The final measured DOC concentration of 28.8mg/l compared to a concentration of 26.4mg/l measured with the TOC analyser yields an error of 9.1%.

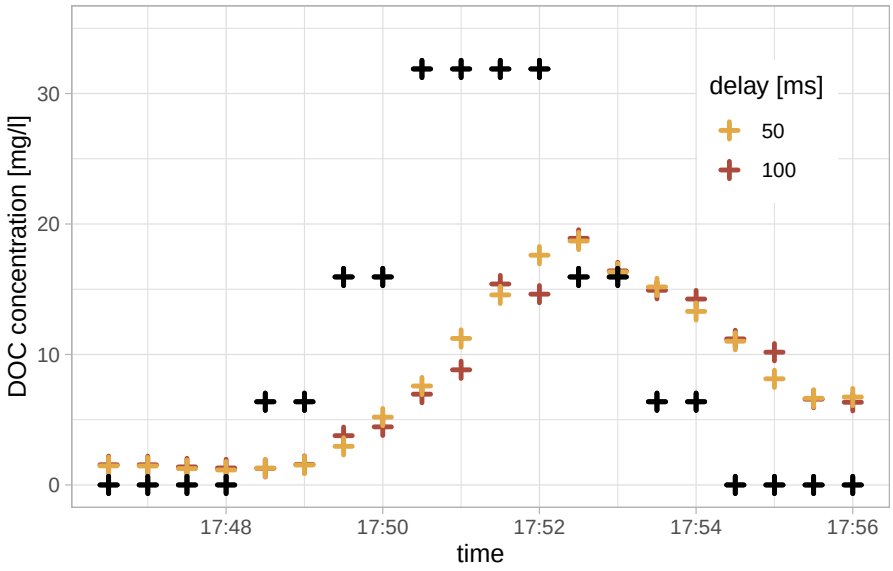

Figure 4.4: Sample 3 with different concentrations was applied to the measurement system. The applied concentrations are plotted in black and the measured concentrations in two colours for different delay times.

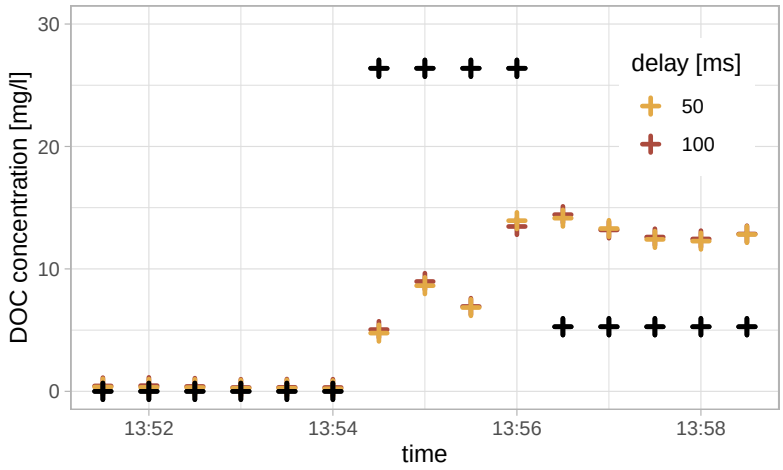

Figure 4.5: Solution 1.1 with different concentrations was applied to the measurement system. The applied concentrations are plotted in black and the measured concentrations in two colours for different delay times.

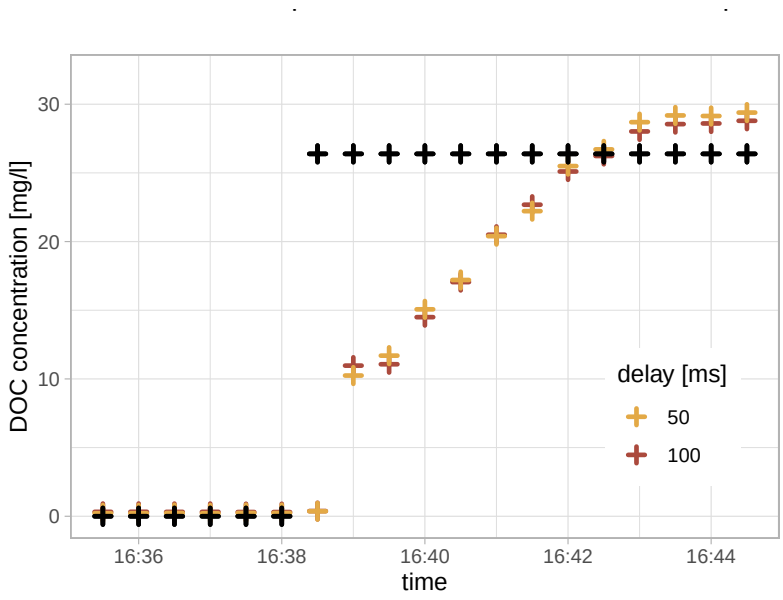

Figure 4.6: First water was applied to the measurement system and then a 50 % dilution of solution 1.1 was applied. Again the applied concentrations are plotted in black and the measured in two colours.

4.4 Test with a Block of Forest Soil

For each irrigation experiment the start and end weight of the spray bottle and the recipient are subtracted to find the applied volume (V_{appl}), the discharged volume (V_{dis}) and the average irrigation intensity. The found values together with the volume obtained by the drop counter (V_{dc}) are presented in table 4.4.

Table 4.4: Measured solution volumes for the irrigation experiments with different measurement techniques.

Experiment	Intensity [ml/min]	V_{appl} [ml]	V_{dis} [ml]	V_{dc}[ml]
(A)	17	319	13	17
(B)	52	421	65	52
(C)	-	-	-	-
(D)	67	500	381	256
(E)	18	165	117	101
(F)	107	502	462	473

For the DOC concentrations again the fluorescence peak integrals of the measured spectra are calculated and the regression function (3.4) is used to convert the integral values into DOC concentrations. For the irrigation experiments the fit parameters of sample 1 are used. In Figures 4.7 to 4.9 the obtained concentrations are plotted over time together with the concentrations measured by the TOC analyser and the volume measured by the drop counter. Experiments (A) and (B) are conducted on the 10.09.2021 and all other experiments are conducted on the 13.09.2021. In the experiments (B),(C) and D the data shows some gaps. In those moments the mirco controller got wet or was moved and stopped recording. For experiments (E) and (F) this problem was fixed. For these two experiments without data gaps the total DOC flux is calculated. Therefore the difference in volume for each time step is multiplied by the DOC concentration of the time step and then the products are summed across the experiment time. This yields 2.5mg DOC for experiment (E) and 10.5mg DOC for experiment (F).

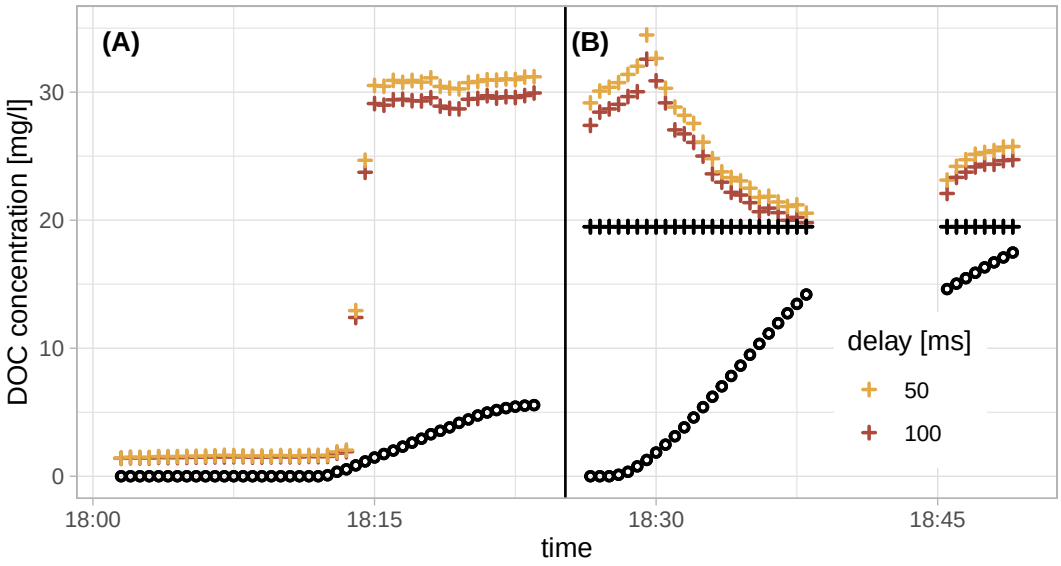

Figure 4.7: The coloured crosses show the DOC concentrations obtained by the spectrometer and the black crosses show the DOC concentration from the TOC analyser. The black circles show the measure volume with an arbitrary unit. The left subplot shows experiment (A) with 17ml/min intensity and the right subplot shows experiment (B) with 52ml/min intensity.

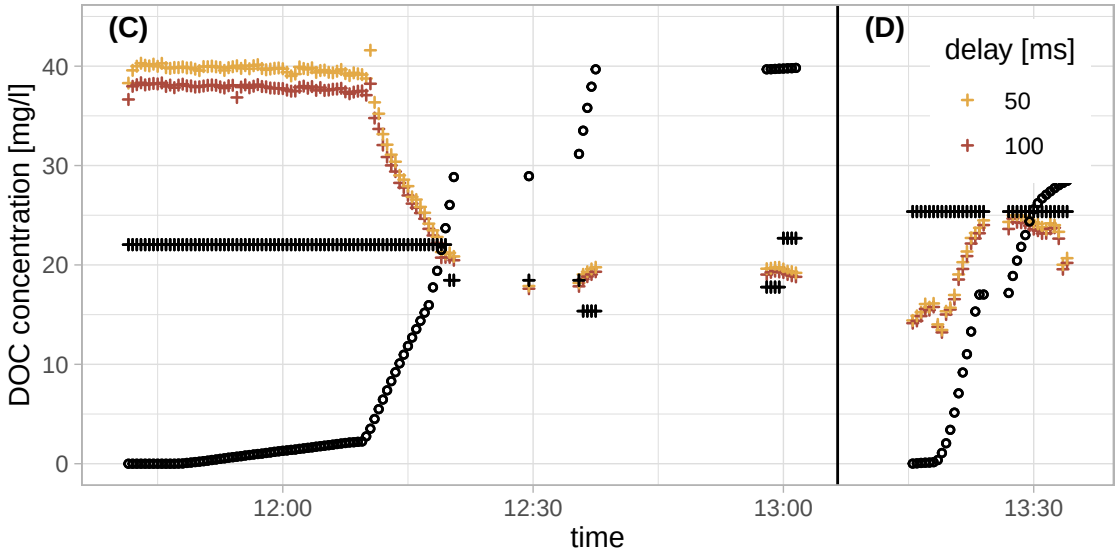

Figure 4.8: The coloured crosses show the DOC concentrations obtained by the spectrometer and the black crosses show the DOC concentration from the TOC analyser. The black circles show the volume measured by the drop counter with an arbitrary unit. The left subplot shows experiment (C) with 60ml/min intensity and the right subplot shows experiment (D) with 67ml/min intensity.

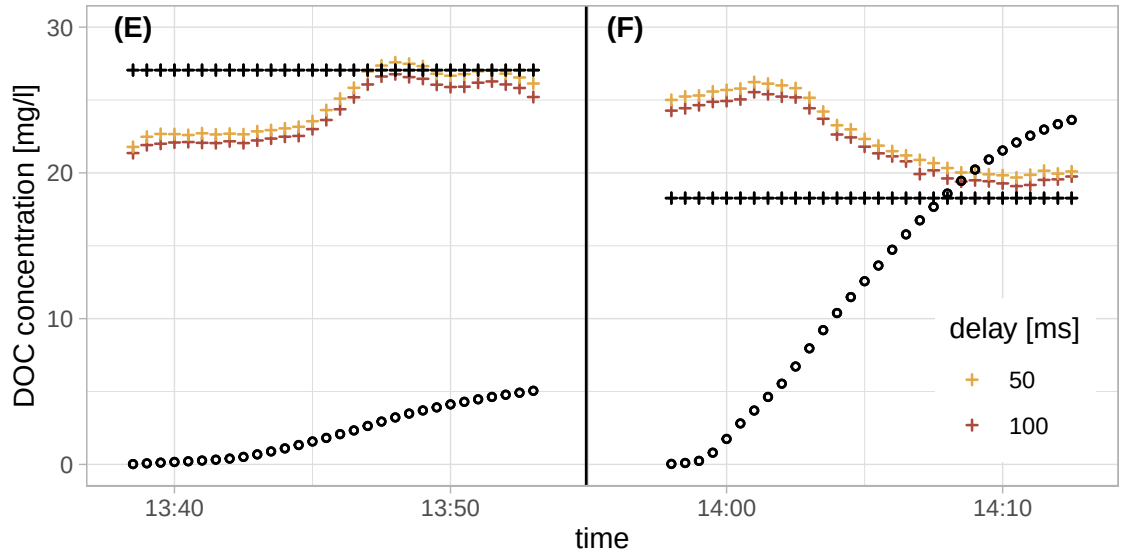

Figure 4.9: The coloured crosses show the DOC concentrations obtained by the spectrometer and the black crosses show the DOC concentration from the TOC analyser. The black circles show the volume measured by the drop counter with an arbitrary unit. The left subplot shows experiment (E) with 18ml/min intensity and the right subplot shows experiment (F) with 107ml/min intensity.

5 Discussion

5.1 Calibration

5.1.1 Calibration Regression

In general the regression function (3.4) yields a good result for all samples and all delay times. The only points that lay far apart are the points for sample 2 with 50% dilution which is probably due to a mistake in the experimental procedure. Furthermore it was seen that the graphs have an upper limit around 100 mgC/l. This is due to the reason that the intensity of the fluorescence signal decrease for high DOC concentrations because of absorbance as written in section 3.2.5. Therefor every integral value can be mapped to two concentrations and the function that associates the integral value with the DOC concentration is a multivalued function with two branches. The branch used for the regression ends for DOC concentrations between 90 and 105mgC/l and the system can thus only measure correctly for concentrations below that limit. The spectrometer is sensitive and can detect even low concentrations of DOC in the sample. The calibration data goes down to as far as 2.7mgC/l which is still recognisable. The expected concentrations are between 20 and 90mgC/l (see section 1.6) and hence the system covers the common concentrations.

The plot 4.1 also shows, that the fluorescence signal depends as well on the type of soil. The curves of sample 1 and sample 3 almost match but the sample 2 which comes from a coniferous forest differs. Hence, the system should be calibrated for every location individually.

5.1.2 Absorbance Measurement

To improve the performance for high concentrations an additional absorbance spectroscopy measurement would be helpful. The absorbance value at least could be used to decide in the range of which branch of the Lambert W function the measured sample lays and thus calculate the right concentration even if its high. Maybe the measured absorbance could even be used to correct the fluorescence signal yielding in a linear relation between the corrected fluorescence signal and the DOC concentration. Finally it could also be possible to deduce the DOC concentration directly from the absorbance measurement which could than be conducted by any other transition wavelength. But as stated before additional material and time would be necessary to test these features.

5.1.3 FDOM Quality

Remarkably is that even though the total DOC concentration of sample 1 and sample 3 differ significantly (see table 4.1) their regression curves almost coincide (see figure 4.1). However, the regression curve of sample 2, which total concentration does not deviate more from sample 1, indeed does differ from the other two curves. As mentioned sample 1 and 3 were taken in deciduous forests whereas sample 2 was taken in a coniferous forest. In section 1.8.2 is stated, that the fluorescence intensity of the soil solution not only depends on the DOC concentration but also on its composition. Every compound of the DOC shows particulate fluorescence behaviour and therefore the fluorescence signal of solutions with different DOC composition may differ even so the total DOC concentration is the same. As the composition of the DOC depends on the litter input it is consistent that the sample from the coniferous site shows another fluorescence intensity for the same concentration than the samples from the deciduous sites. Consequently, the system has to be calibrated separately for every new location as the fluorescence to DOC relation depends on the soil composition and thus changes with space. The working hypothesis is that this relation does not change significantly with time at a fixed place. However, this is still an open question and it is recommended to take control samples to the laboratory regularly when using the in-situ system to check is hypothesis.
Another open question is how much of the fluorescence signal really comes from DOM and how much from other compounds in the solution for example POM. In continuation this could be checked by removing everything but DOM from the solution (i.e. with a membrane filter) and compare the fluorescence result with the unfiltered one.

5.1.4 Intensity Calibration

The Raman scatter peak of water is not identifiable for delay times below 200ms. However, especially for high doc concentrations with a delay time of 200ms or higher the image sensor of the spectrometer gets oversaturated. Furthermore when measured simultaneously the fluorescence peak overlaps with the Raman scatter peak and thus can not be identified. Thus, the Raman scatter peak is not useful for this purpose. It could be helpful to compare different setups when measuring very low DOC concentrations with high delay times.
As the calibration with the artificial soil solutions yields good results and only one instrumental setup is used anyway, the calibration with a standard reference material is considered dispensable.

5.2 Drop Counter Evaluation

The expected intensity in the field is between 0 and 120mm/h and thus is covered by the range of the drop counter which lays between 0 and 400mm/h according to

the manual, but does exceed the high precision limit of 50mm/h (Meter Group AG, 2020).
Additionally to the expected statistical error in the experiments there was a systematical error on the measured volume which underestimates the volume in 86% of the case. Only in one case the measured volume comes close to 100% and only in one case above. If this two special cases are cancelled out the systematic error is -17% and the statistical error $\pm 5\%$. The applied volume of 5 and 10ml/min correspond to a precipitation height of 44 or 88mm/h. Thus, even so the 5ml/min lay within the range of high precision and the 10ml/min do not, both comply equally with the precision of $\pm 5\%$.
For the systematic error several reasons can be mentioned:

1. The instruction by Metergroup to check the drop counter (Meter Group AG, 2021) states, that the drop counter should be within $\pm 2^\circ$ of dead level to guarantee that all the drops hit the gold pins. With the used water level it is not ensured that this precision is accomplished.

2. Since the same micro controller reads the signal from the drop counter and the spectrometer the drop counting is interrupted every time a spectrum is measured. This is probably the main reason, why the volume is underestimated by a similar amount most of the time.

3. Furthermore if the water falls directly into the flared hole or big portions of water are applied to the funnel the drops are not separated properly at the flared hole and thus cannot be counted individually.

4. Finally the proposed drop volume by the manual might be too small and a recalibration of the drop counter should be considered.

Approaches to identify and solve these problems are the following:

1. To achieve the required level a plumb could be used or even better a digital level with a levelling disc.

2. To test if the spectrometer measurement actually affects the volume accuracy another code could be written that only reads the drop counter without interruption. If this improves the result, two micro controllers should be used for the two instruments.

3. In order to provide that the drops are separated at the flared hole one has to ensure, that the samples fall on the funnel in small drops and not directly into the hole. Maybe the hole has to be shielded or the drops dispersed in a way.

4. If all the previous steps do not lead to a satisfying result, the drop counter should be recalibrated to determine the correct drop volume for different intensities.

5.3 Flow-through Test

The tests with the flow-through cuvette revealed that it is possible to measure the volume of a solution and its DOC concentration automatically with a high frequency of 2min^{-1}. The drops were counted throughout the whole time and induced changes in concentration could be detected.
However, figures 4.4 to 4.6 show that there is a time delay between the applied and the measured concentration. Figure 4.4 and 4.5 additionally indicate that the solutions disperse in the cuvette and the solution that remains inside of the cuvette is getting mixed with the solution flowing in instead of being pushed out. Simulation 5 shows that it takes 4:30 minutes and about 45ml until the concentration stabilises inside of the cuvette when applying a constant concentration to the system (see Figure 4.6). The cuvette has an inner volume of 3ml and all the tubes together have a volume of about another 3ml. Thus the volume needed to rinse the system is much bigger than the actual volume of the system, indicating that the solution inside the system is not only pushed out by the incoming solution but mixes with the new solution and therefore remains for a longer time.
Simulation 5 also shows that the spectrometer measures the DOC concentration with an accuracy of 9.1%, when the incoming concentration is constant, even so the calibration was done with another solution. The solution 1.1 was prepared using the same soil sample as solution 1 which could be a sign, that DOC composition does not change quickly for soil solutions from the same place.
The spectrometer only needs a small window of less than 1cm to measure the spectral response of the solution. The flow-through cuvette used has a inner height of about 4cm. Using a customised cuvette with a shorter height would reduce the mixing of solution already in the cuvette and incoming solution and like this decrease the effect of delay and dispersion. It could also be taken into account to improve the flow-through system by adding a valve or a pump to the tubes and thus get more control of the inflow and outflow. However, up to now it was not possible to build a working system with valves, because that would require an additional opening on the cuvette for leaving air, which is not existent on the used one. Therefore the system with a siphon and without valves yields the best result so far.
For all the tests, the measurements with a delay time of 50ms or 100ms yield basically the same result which demonstrates that the dependence on the delay time is well described by the regression function 3.4. Only for the high concentrations above 26mgC/l in figure 4.6 the deduced concentrations for the delay time of 100ms lay 2% below the concentrations for a 50ms delay time. A cause for this difference is not apparent.

5.4 Test with Forest Soil

5.4.1 Volume measurement

During the irrigation experiments three solution volumes where measured: Firstly the water volume applied to the soil with the spray bottle (V_{appl}), secondly the solution volume that flows out of the siphon into the recipient (V_{dis}) and thirdly the volume that is measured by the drop counter (V_{dc}). For all experiments expect experiment (C) the volume values are displayed in table 4.4. Experiment (C) was a very long experiment of 34 minutes and of about 2l water applied. The spray bottle had to be refilled and the recipient changed several times and therefore it was not possible to measure V_{appl} and V_{dis} precisely. Furthermore the drop counter was interrupted several times and thus a total V_{dc} is not available either.
For experiment (A) and (B) V_{appl} is much bigger than V_{dis}. This is due to water retention capacity. The amount of discharge depends on the soil moisture content in addition to the irrigation intensity. Therefore in the experiments without preceding experiments a large part of the applied water can be hold within the soil and the discharge volume is reduced. This is also visible in figure 4.7 (A). In the very first experiment there is no discharge during the first 11 minutes of irrigation.
Table 4.4 furthermore shows that for experiment (E) and (F) V_{dis} is almost as big as V_{appl}. In these two experiments the soil was already thoroughly moistened by the two experiments directly before. The remaining difference is probably due to the delay of the discharge and an insufficient waiting time before measuring V_{dis}. Figure 4.9 also shows that the discharge starts almost immediately after the start of irrigation.
Finally the accuracy of the drop counter in this setup is evaluated. For all experiments (except experiment (C)) the drop counter measures the volume with an accuracy of $90 \pm 20\%$. However, in experiments (B) and (D) the drop counter is interrupted too and therefore misses part of the discharged volume. In the remaining experiments the drop counter determines the discharge volume with an accuracy of $105 \pm 20\%$. In section 4.2 it is revealed that most of the time the volume is underestimated by the drop counter. The overestimation in this case is probably due to the delay of the discharge which reduces V_{dis} and thus compensates the underestimation produced by the drop counter. After all, when working without interruptions the drop counter roughly hits the discharged solution volume.
To guarantee a continuous operation of the drop counter and the rest of the measurement system, all electronic parts and cables have to be fixed and protected from splashing water.

5.4.2 DOC measurement

The results of the test with forest soil (see section 4.4) show that in general the DOC concentration increases when the discharge is low and decreases with high discharge. This can be observed throughout the whole experiment set.

In experiment (A) when the soil is saturated sufficiently so that discharge starts the DOC concentration jumps very quickly to about 30mg/l and then remains constant for a constant discharge (see figure 4.7 (A)). Quickly after the discharge rises in experiment (B) the DOC concentration falls to a concentration of 20mg/l. Then there is a data gap, but when the discharge slightly declines in the end of (B) the DOC concentration slightly increases again.
Between experiment (B) and (C) three days passed by. In this time the holes in the plastic boxed got blocked by dried sediment. Therefore in the first 30 minutes of experiment (C) the discharge was very low of about 1ml/min even so 60ml/min were applied. In this time the measured DOC concentration was the highest with about 40mg/l. Once the blockade was removed with a little stick the discharge rose immediately to 22ml/min as all the water stored in the box drained. Again with the increasing discharge the DOC concentration drops to about 20mg/l. Unfortunately during the rest of experiment (C) the system was not working properly. With the little data obtained it is hard to interpret anything, but it was observed, that the discharge remained high and at the same time the DOC concentration stayed low.
Contrary to expectations in the beginning of experiment (D) the DOC concentration rises again up to 25mg/l even so water is applied with an intensity of 67ml/min. This is probably due to the reason that the solution that flowed into the cuvette during experiment (C) had a very low DOC concentration as a large water volume was applied and discharge was very high after removing the blockade. However, between experiment (C) and (D) for one hour no new water was applied and thus at the end of experiment (C) and in the beginning of experiment (D) the discharge was relatively low, which could explain the increase of the DOC concentration. In the end of (D) the concentration declines again which is in accord with the hypothesis of negative correlation of discharge and DOC concentration. It should be remembered that in section 4.3 it was found that there is a delay about 4:30 minutes and 4.5ml solution starting from the solution falling onto the drop counter until it is measured by the spectrometer. This additionally explains why the DOC concentration does not always respond to the rising discharge immediately.
In the experiments (E) and (F) the same process can be observed. In experiment (E) with a low intensity of 18ml/min the DOC concentration starts rising after a time of 6:30 minutes a discharge of roughly 30ml and reaches a plateau of about 27mg/l after 8:30 minutes and about 50ml discharge. In experiment (F) with a high intensity of 107ml/min the DOC concentration starts falling after a delay time of 5:00 minutes and a volume of about 160ml and reaches a plateau of 20mg/l after 9:00 minutes and a volume of about 330ml. This indicates that there is rather a constant delay time, than a constant delay volume.
In section 1.6 it is mentioned that the annual flux of DOC through the forest soil correlates with the precipitation. To proof if this statement can be confirmed by these experiments for experiment (E) and (F) the total DOC flux is calculated (see section 4.4). This results in that for higher V_{appl} also the total DOC flux is higher but as the concentration decreases with increasing intensity this correlation is not a proportional one.

Comparison of measured DOC concentration with TOC Analyser

As the solutions that were measured with the TOC analyser were sampled during the whole time of one experiment they are expected to have a DOC concentration that lay in the range of the DOC concentrations measured with the spectrometer during the respective experiment. However, for experiments (B) and (F) the concentration measured with the TOC analyser lies below all concentrations measured with the spectrometer and for experiments (C),(D) and (E) the concentration measured with the TOC analyser lies above all concentrations measured with the spectrometer. In experiment (C) there are to many data gaps top make a comparison. In experiments (B) and (D) the data gap could account for the deviation, but in experiments (E) and (F) there must be another reason.

Comparison of the delay times

Like in section 5.3 the concentrations measured with the two delay times generally show the same dynamics. And again for high DOC concentrations the value obtained with 50ms delay is higher than the one obtained with 100ms seconds delay. This deviation increases with increasing concentrations. However, as this is a systematic observance it can probably be corrected by a new calibration with sample from the corresponding soil.

6 Conclusion

The general conclusion of this thesis is that it is possible to measure the volume of the soil solution and its DOC concentration with the designed setup. Furthermore the cost of the whole spectroscopic unit lays below €500, which is definitely cheaper than all comparable commercial solutions. However, the in-situ measurement system has its limitations: The measurement range for the flow rate lays between 0 and 400mm/h and thus covers the expected flow rate of 0 to 120mm/h in temperate forest. Yet, very high intensities above 50mm/h lay exceed the high precision limit of the drop counter.
The effective range for the DOC concentration is between 0 and 100mgC/l and therefore also covers the expected DOC concentrations of 20 to 90mgC/l in the O horizon of forest soils. For the irrigation experiments performed in this thesis the DOC concentrations indeed lay between 10 and 40mgC/l. Using a smaller pathway or by adding a convenient absorbance measurement the upper limit for the concentration measurement could even be increased.
For the drop counter the manual indicates a accuracy of $\pm 5\%$ for the measured volume. In the experiments the measured volume additionally shows an systematic error of -17% when compared to the volume that was applied to the drop counter. In section 5.2 reasons and solutions for this error are discussed.
When the DOC concentration is stable the measurement with the spectrometer yields an error of 9.1%. However, the bigger problem about the accuracy of the DOC measurement is that as the solution flows through the cuvette, there is an effect of delay and dispersion on the concentration measurement. When a solution with constant DOC concentration is applied it takes between 4:30 and 9:00 minutes and between 45 and 330ml of solution applied until the signal of the spectrometer stabilises. This could be improved by using a shorter cuvette.
In order to respond on sub question 2 how much the results depend on place and time basically two questions have to be answered. First, how much does the composition of DOC change with place and time and secondly how much does the fluorescence signal depend on the DOC composition. For both questions this thesis only gives an idea. The calibration with soil samples from different places which supposedly show different DOC composition show that for different conditions in the forests the fluorescence per carbon ration changes which is probably due to changes in the DOC composition. The two samples from the deciduous forest though show a very similar fluorescence per carbon ratio, indicating that the composition does not necessarily change with place but with the conditions in the forests. The question if the results change with time cannot be answered thoroughly as no long term experiment was performed. The fact, that the concentration of solution 1.1, which was prepared

from the same bulk sample as solution 1 some weeks later, can be approximated using the calibration done with solution 1 already gives a hint that for a fixed place there are now severe changes in DOC composition over time. This can be used as a working hypotheses until the contrary is demonstrated.
With the calibration method a way is found to deduce DOC concentrations from the fluorescence intensity for the common concentration interval. The plots from the experiments in section 4.3 and 4.4 show that the chosen delay times of 50 and 100ms are applicable for all emerging concentrations. The two delay times increase the consistency of the measurement and the similar results demonstrate that the linear dependency on the delay time is well-described by the regression function (3.4).
Michalzik et al. (2001) claims that the annual DOC load correlates with the annual precipitation. Section 4.4 gives evidence that the DOC concentration decreases with increasing discharge. However, the decreased concentration does not compensate for the increased discharge and the total DOC load is still higher for higher discharge. Thus, this leads to the interpretation, that the DOC load does grow with growing precipitation, but it is not a linear growth.

6.1 Outlook

In order to make the system ready for operation in the field two more steps have to be fulfilled:

- The whole system needs a battery or another energy source for supply in the field.
- A frame must be built that fixes all the electronics and protects them from getting wet and makes it possible to transport the system.

When installing the system in the forest it is recommended to evaluate the DOC concentration measurement by laboratory samples and if necessary always measure the DOC by a combination of in-situ spectroscopy and sample solutions, where the sampling provides a high accuracy of the concentration and the spectroscopy a high resolution which together will yield a high resolution with high accuracy. It is also possible that the evaluation gives evidence that the fluorescence intensity per carbon is relatively constant over time so that only one calibration process in the beginning is necessary to produce reliable results.
There are several considerations how to improve the measurement of the flow rate and the DOC concentration.

- The accuracy of the volume measured by the drop counter can be improved following the section 5.2.
- By comparison of filtered and non-filtered soil solutions (with a 0.45µm membrane filter) how big the influence of POM and other particles is on the fluorescence of the soil solution.

- The design of a customised flow-through cuvette could reduce the delay and dispersion effects on the concentration measurement.
- The addition of an absorbance measurement could yield in more reliability in the concentration measurement and could increase the upper limit for the measurement of high DOC concentrations.

Finally more investigation on the composition of DOC and the fluorescence of the different fractions in the laboratory and in the field is required in order to create a complete picture of the dynamics of DOC in the O horizon of forest soils.

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List of Symbols

Abbreviations

Name	Acronym
Carbon	C
Carbon dioxide	CO_2
Chromophoric dissolved organic matter	CDOM
Dissolved organic carbon	DOC
Dissolved organic matter	DOM
Fluorescent dissolved organic matter	FDOM
Formultning layer	F layer
Global carbon cycle	GCC
Humus layer	H layer
Inter-Integrated Circuit	I^2C
Lambert W function	$W(x)$
Light-emitting diode	LED
Litter layer	L layer
Organic horizon	O horizon
Particulate organic matter	POM
Real time clock	RTC
Serial Peripheral Interface	SPI
Soil organic matter	SOM
Specific ultraviolet absorbance	SUVA
Total organic carbon	TOC
Ultraviolet-visible	UV-VIS

Physical Quantities

Name	Unit	Symbol
Concentration	[mgCl^{-1}]	c
Correlation factor 1	[mgl^{-1}]	α
Correlation factor 2	[ms^{-1}]	β
Correlation factor 3	[ms]	γ
Delay time	[ms]	d
Fluorescence intensity	[W/m^2]	F
Light intensity	[W/m^2]	I
Volume applied	[ml]	V_{appl}
Volume discharged	[ml]	V_{dis}
Volume drop counter	[ml]	V_{dc}

Declaration

Hiermit erkläre ich, dass die Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel angefertigt wurde.

Ort, Datum Unterschrift