



**University of  
Zurich**<sup>UZH</sup>

# Spatial and Temporal Variability in Stream Chemistry in a Temperate Intermittent Stream

GEO 511 Master's Thesis

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**ABSTRACT**

Intermittent streams, i.e. streams that experience a repeated rewetting and drying cycle, have been neglected in research up until recently, despite their importance in regional to global biogeochemical and water cycles. They make up over 50% of the global river networks, a number expected to increase further in the future due to climate change and human impact, which is why further research into the functioning of these stream network is crucial. The aim of this thesis was to investigate the response of a small intermittent stream catchment in the vicinity of Zurich to rainfall events. More specifically, it was studied if and how stream chemistry changes over the course of a rain event, how these changes in chemistry differ spatially across the catchment, and whether these changes differ over the course of the rewetting period. It was found that streamwater chemistry did change over the course of a rainfall event, with a tendency to doing so less strongly over the course of the rewetting period. To answer these questions, streamwater samples were taken on three locations distributed over the catchment during five rain events in late fall/early winter of 2018, which were subsequently analyzed on their isotopic composition  $\delta^{18}\text{O}$ , EC, and DOC, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, and Ca<sup>2+</sup> concentrations. No traditional first flush behavior could be observed. The change in chemistry happened in a more erratic way, with strong fluctuations in some solutes during some events, and much more calm and constant in some solutes during some events. However, a flush-type behavior could still be made out, as E1 exhibited the widest range of solute concentrations. Concentration-wise E1 was generally among the highest of events, but as there were events later on in the sampling season that showed equally or higher concentrations E1 cannot be said to have the biggest flush. The extent of the flushing of solutes did not correlate well with precipitation intensity, and is more likely to be correlated to hydrological and groundwater connectivity of the stream network. The composition of dissolved carbon in the streamwater was found to be quite stable throughout the sampling season, but was diluted with groundwater high in inorganic carbon once the groundwater had reconnected with the stream network. In addition to the temporal variations found in streamwater chemistry change, said change also varied spatially across the catchment, whereby the extent of the variability depends on the solute. The results of this thesis could be helpful to decision makers in the management of intermittent streams, as well as in water quality management, as the more we know, the better we know how to manage and conserve intermittent streams.

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### LIST OF ABBREVIATIONS

$\delta^{18}\text{O}$	measure of the ratio of the stable isotopes $^{18}\text{O}$ and $^{16}\text{O}$ as compared to a standard
$\delta^{13}\text{C}$	measure of the ratio of the stable isotopes $^{13}\text{C}$ and $^{12}\text{C}$ as compared to a standard
(D)OC	(dissolved) organic carbon
(D)IC	(dissolved) inorganic carbon
EC	electrical conductivity
UV254	reflectance measured in UV wavelength at 254 nm
wl	water level
RG	rain gauge
A/B/C	Isco sampling locations A, B, and C
SSS	single stage samplers used for snapshot sampling
E1-E5	sampling campaign event numbers
$\text{K}^+$	potassium ion
$\text{Ca}^{2+}$	calcium ion
$\text{Cl}^-$	chloride ion
$\text{NO}_3^-$	nitrate ion
$\text{SO}_4^{2-}$	sulfate ion

## 1 INTRODUCTION

### 1.1 WHAT IS AN INTERMITTENT STREAM

Intermittent streams or temporary rivers are rivers that periodically cease to flow. They are usually depicted as dashed lines on maps (figure 1.1) and occur all over the world. During cessation of flow, there can be a presence of surface water in isolated pools, an extensive pool system, or total loss of all surface water (Stubbington et al., 2017). Intermittent headwater streams make up a majority of stream length, are the source of water for downstream ecosystems. According to Datry et al. (2014), intermittent streams constitute more than half of the global river network, and are therefore among the most common and most hydrologically dynamic freshwater ecosystems (Larned et al., 2010). They occur in most terrestrial biomes, and are possibly the dominant system in arid, semi-arid, and Mediterranean-climate regions, but are common in temperate regions as well (Stubbington et al., 2017). Streamflow intermittence can occur throughout the whole stream network, however, in temperate or humid climates the headwater streams are more likely to experience periodic flow cessation and drying (Gonzàles-Ferreras & Barquín 2017; Hale & Godsey, 2019).

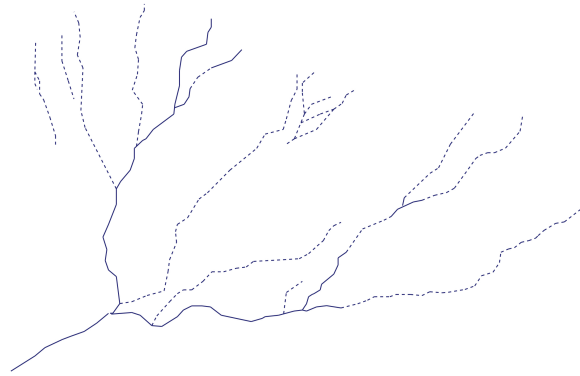


Figure 1.1 Sketch of an intermittent stream as they are typically represented on maps. The dotted lines are stream reaches that experience periodic cessation of flow. Such streams make up more than 50% of the global river network and occur all over the world.

### 1.2 IMPACTS OF CLIMATE CHANGE AND HUMAN INFLUENCE

The number of streams experiencing at least some period of drying, and the severity of intermittency is expected to increase due to climatic change and the associated increase of frequency of drought periods in many areas, as well as increasing water abstraction and impoundment (Gleick, 2003; Palmer et al. 2008; Larned et al., 2010; Döll & Schmid, 2012; Datry et al., 2014; Stubbington et al., 2016). Human impact and the thus anthropogenic flow intermittence is a growing environmental problem, which might lead to fishery declines, loss of migratory pathways, changes in nutrient cycles, and a diminution in the efficacy of ecosystem services (Jackson et al., 2001; Xenopoulos et al., 2005; Larson et al., 2009; Larned et al., 2010). Due to this expected change, there is an increasing need for research on these systems (Larned et al., 2010). As a matter of fact, despite their importance for global water and nutrient cycles, or their significant ecosystem services, research on the hydrology of intermittent river systems, their biogeochemical functioning, and their ecology has been limited, leaving us with a severe shortage of information (Larned et al., 2010; Shumilova et al., 2018). Despite the recent increase in intermittent stream research, the understanding of the differences in biogeochemical cycles between intermittent streams and perennial streams is still limited. Observations at small or intermediate scales may be promising to advance our knowledge on these fluxes and understanding of the spatial complexity of biogeochemical processes throughout the stream network (McGuire et al., 2012; Datry et al., 2014).

### 1.3 THE ROLE OF INTERMITTENT STREAMS

Intermittent streams are essential to the integrity of their entire river networks (Larned et al., 2010; Acuña et al., 2014; Datry et al., 2014; Shumilova et al., 2018). They are the entry point for most of the materials moving through a river network (McGuire et al., 2012; Blaen et al., 2016). Intermittent streams thus provide important links in the hydrological cycle, as they connect water stored in soils, aquifers, snowpacks, glaciers, vegetation, and the atmosphere (Larned et al., 2010), and biogeochemical processes and cycles. Inclusion of intermittent

headwater streams can significantly affect global or regional carbon and nutrient fluxes (Battin et al., 2008; Shumilova et al., 2019), as headwater streams represent the key sites of nutrient retention, but little is known about temporal variation in this important process (von Schiller et al., 2008). Intermittent streams are also important habitats. They are home not only to generalists, but also to resilient taxa that recolonize their habitat once it becomes available again during the drying and rewetting cycle, and specialists with high endemicity due to their isolation during the dry(ing) period (Larned et al., 2010; Datry et al., 2014; Stubbington et al., 2017). Intermittent streams thus provide a wide range of ecosystem services that are important to humans and the natural environment (Wigington et al., 2005; Larned et al., 2010; Stubbington et al. 2017; Wohl, 2019), however, this is still largely unrecognized to most people not involved in this specific field of research.

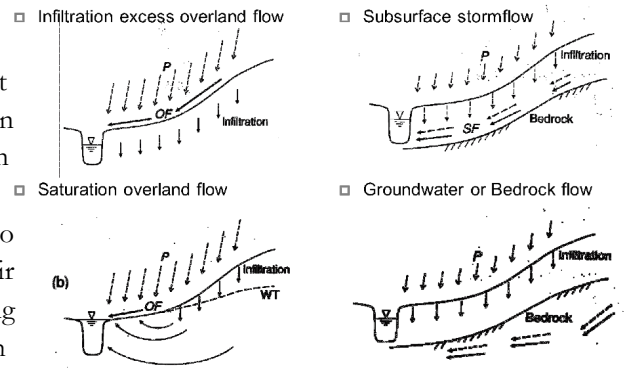


Figure 1.2 Different types of overland flow according to Brutseart (2005), which each influence the streamflow pathways and thus the stream chemistry a little differently.

According to Shumilova et al. (2018), rewetting events in intermittent streams play an important role in the global biogeochemical cycling of nutrients and organic matter. Flow intermittence causes unique flow regime dynamics along the stream, as many stream networks are not controlled by continuous springs and can expand drastically in response to floods or changing groundwater levels (Larned et al., 2010; van Meerveld et al., 2019). The rewetting of streams leads to high ecosystem respiration rates (mean respiration increase of 32 to 66-fold upon sediment rewetting and other biogeochemical processes (Romaní et al., 2006; von Schiller et al., 2019). It has been stated that such respiration pulses could even contribute significantly to annual CO<sub>2</sub> emissions from the global stream network, as a single pulse could increase emissions by 0.2 to 0.7 % (von Schiller et al. 2019). Streambeds of intermittent rivers accumulate organic matter, nutrients, and terrestrial plants during dry periods. When flow resumes, and the wetted stream sections expand, these are suddenly transported downstream. The transport of this organic matter and other nutrients in both dissolved and particulate form increases their concentrations and can exceed base flow concentrations by orders of magnitude (Baldwin & Mitchell, 2000; Bernal et al., 2005; Datry et al., 2014). Particularly, concentrations of phosphate or inorganic nitrogen (e.g. in the form of nitrate) increase after rewetting, whereby the effect of phosphate release is usually more long-term than for nitrate (Baldwin & Mitchell, 2000; McComb & Qiu, 1998; Song et al, 2007). For carbon compounds that are leached from organic materials, with terrestrial inputs dominating this supply of DOC (Palmer et al. 2001), the concentrations can become so high and lead to hypoxic blackwater events further downstream (Baldwin & Mitchell, 2000; Hladyz et al., 2011). The response of stream chemistry to rainfall events in intermittent streams is thus crucial to understanding the export of dissolved and particulate solutes from a catchment, as such times are biogeochemical „hot moments“, with sediment and nutrient concentrations in the advancing fronts often being greater than those found in perennial rivers – they have been recognized as biogeochemical reactors (Larned et al., 2010; Fovet et al., 2018; Shumilova et al., 2018). As such, rainfall events have major implications for biogeochemical cycles at local and regional scales and they provide an excellent opportunity to study the hydro-biogeochemical functioning of catchments. (Butturini et al. 2008).

#### 1.4 FLOW PATHWAYS

How stream chemistry changes during an event depends on the flow pathways. Precipitation can fall directly on the stream surface or on saturated areas and then flow to the stream (figure 1.2). In perennial streams, this

generally leads to a dilution of most solutes because of the low concentrations in rainfall. Precipitation intensities may also be higher than the infiltration rates causing overland flow as well, but this is generally limited to undisturbed climates in humid areas. Rainfall may also infiltrate into the soil and flow through the soil to the stream (figure 1.2). This can increase concentrations of some solutes such as nitrate and potassium because the concentrations of these solutes are generally higher in the soil than in the groundwater. Alternatively, the infiltrating water may push out more groundwater, which should lead to a small change in concentrations compared to the pre-event concentrations because groundwater is the dominant flow component of baseflow (figure 1.2). Changes in isotope ratios and stream chemistry can help us determine the main flow pathways and thus to better understand what causes intermittent streams to flow.

In the same way stream chemistry changes depend on the flow pathways do flow pathways depend on antecedent conditions of rainfall, soil water, and groundwater levels (Tromp-van Meerveld & McDonnel, 2006). The dependency of runoff due to rainfall on antecedent moisture conditions is a proxy for overall hydrologic connectivity among hillslopes, meaning that during wet conditions, and thus a high degree of connectivity, a much larger portion of the catchment contributes to surface runoff as compared to dry conditions when the hydrologically active zones are minor (von Freyberg et al., 2014). Therefore, depending on the dryness of the soil, drought period prior to rainfall, and, relating to that, the level of groundwater, different flow pathways will be activated, leading to a varying stream network, as the water availability in the riparian area affected the relationship between rainfall inputs and stream runoff (Butturini et al., 2002). Dry periods such as summer see a decrease in groundwater levels, and hydrologic connectivity between surface water and groundwater is lost (Romaní et al., 2006), so groundwater first has to be re-filled by the rain in fall and early winter (Butturini et al., 2002). With increasing groundwater levels, a more extended stream network is obtained, as the water doesn't just run off into the riparian groundwater compartment but can runoff as surface flow (Romaní et al., 2006), whereby size, timing, and intensity of the precipitation strongly influences the extent of the hydrological connectivity (Welter & Fisher, 2016). Rainfall events during wet conditions thus results in overland flow consisting of the precipitation itself, with higher stormflow values observable than during rain events on dry conditions, but also the hillslopes contribute to streamflow (Penna et al. 2011). The fraction of rainwater in the surface runoff are therefore larger during dry conditions, as the overland flow consists mainly of direct channel precipitation; during wet conditions, however, groundwater and hillslope soil water contribute the main part of the surface runoff (Penna et al., 2015). Field studies performed during this hydrological transition from summer drought to the fall humid period and on streams with abrupt changes in discharge and/or groundwater levels are often avoided as they are said to be a source of noise that makes the interpretation of the results far more difficult, however, such hydrological changes are vitally important to understanding the hydrological and chemical functioning of catchments (Romaní et al. 2006).

### 1.5 OBJECTIVES AND HYPOTHESES

Therefore, in this thesis, I will investigate 1) how stream chemistry changes over the course of rainfall events (small-scale temporal variability) when different stream reaches of an intermittent stream begin to flow and become connected, 2) how these changes vary within a catchment (spatial variability), and 3) how these changes vary over the course of the rewetting period (longer-term temporal variability) (see figure 1.3 experiment-idea for an illustration of objective points one and two). This type of research will be helpful to decision makers in the management of intermittent streams (Datry et al., 2014), as well as in water quality management (Wigington et al., 2005), as the more we know, the better we know how to manage and conserve intermittent streams. The changes in stream chemistry are expected to depend on the size and intensity of the event, the duration of the dry period prior to the event, the dominant sources of streamwater (i.e., flow pathways), and the sequence in which the stream reaches connect. In order to see if the first rainfall events that causes the stream to connect



and flow lead to the largest flushing of nutrients, the stream chemistry response was compared for five events. More specifically, this work was undertaken based on the following hypotheses:

1. Streamwater chemistry will change over the course of a rainfall event.
2. This change will happen at the onset of rain due to either flushing of solutes or dilution by the rainfall.
3. The first flush will be largest for the first rainfall event after a long period of drought (i.e. summer 2018) due to the accumulation of material in the stream bed.
4. The extent of the first flush will be correlated with rain intensity; changes in concentrations are expected to be smaller during low intensity rainfalls
5. The changes in streamwater chemistry will differ for different tributaries and typically perennial and intermittent stream sections.
6. Dissolved carbon in the streamwater will be primarily organic in the beginning of the sampling season due to the accumulation of plant litter, which will then be washed out and also allow for more inorganic carbon in future events.

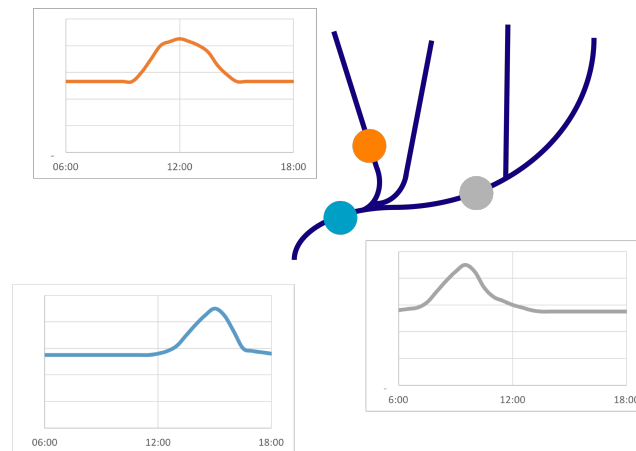


Figure 1.3 The idea behind experiment setup is the following: three locations (blue, orange, and grey dots) were chosen to investigate spatial variability within the catchment. For these measurement sites, small-scale temporal variability over the course of a rainfall event was studied for five events during the fall/winter rewetting period in order to assess larger-scale temporal variability.

## 2 STUDY SITE DESCRIPTION

The Diebis Bach is a small first-order intermittent stream situated on the south-west facing slopes of the Üetliberg in Stallikon ZH (figure 2.1). The stream drains a very small (ca. 0.4 km) forested catchment and flows into the Reppisch. The elevation of the catchment ranges between 540 and 760 m above sea level (asl) (swisstopo 2019a).

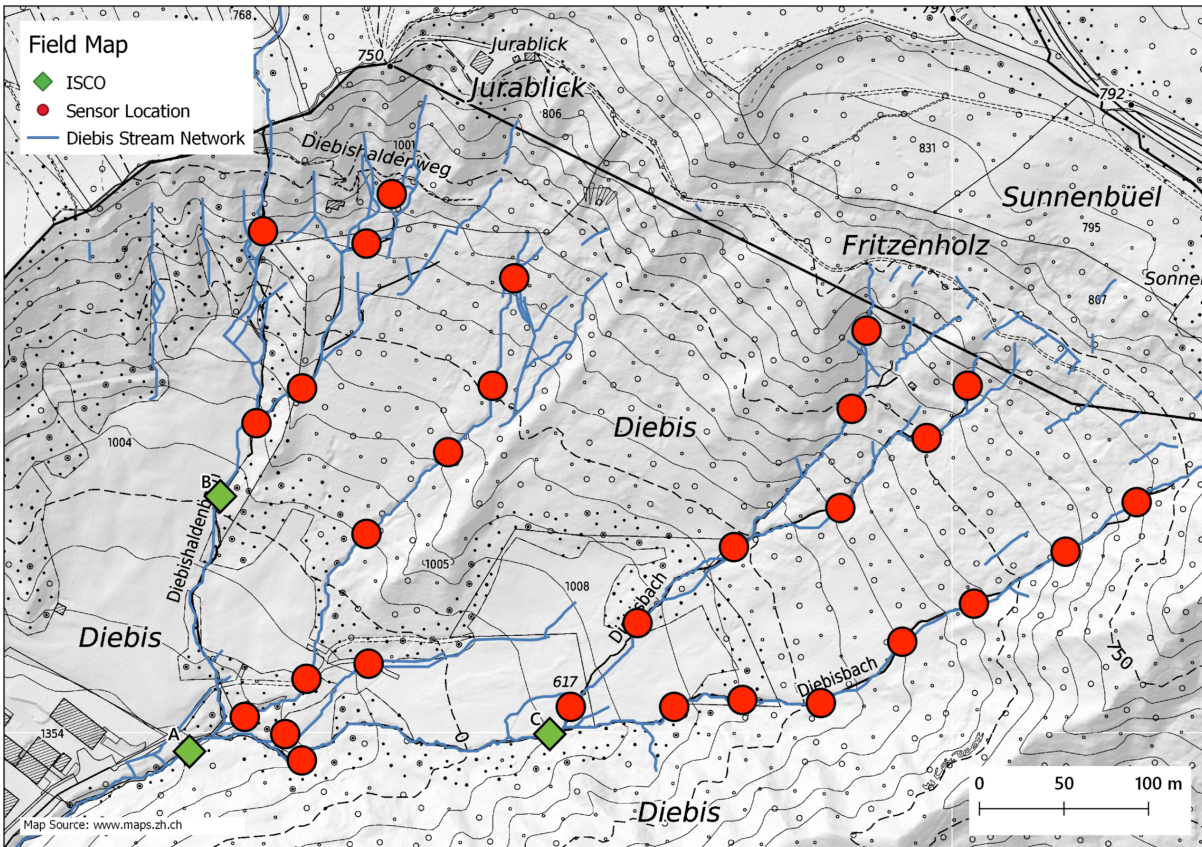


Figure 2.1 Field map of the Diebis catchment in Stallikon, ZH. The blue lines represent the stream network, the green diamonds the three main Isco sampling locations A, B, and C, while the red dots represent the locations of the 29 single stage samplers. The SSS take snapshot samples upon onset of flow, while the Iscos take samples at a certain interval to monitor the temporal variability throughout an event.

The climate is temperate, with an average temperature of 1.2°C in winter (December to February) to 18.5°C in summer (June to August) over the last 15 years (MeteoSchweiz, 2019a). The mean precipitation amounts to around 1000 mm per year (Niederschlag Regenmesser Birmensdorf ZH541). The fall 2018 study period followed a particularly dry (168.8 mm of precipitation between June and August vs 353.8 mm on average over the last 15 years) and hot (average temperature of 21.6°C vs 18.5°C on average) summer, with summer temperatures being the highest since the beginning of measurements in 1864 (MeteoSchweiz, 2019a & 2019b). Even at the outlet, the stream had dried up by early August. The geology in the catchment is largely made up of upper freshwater molasses, which contains a lot of limestone affecting the stream chemistry (swisstopo 2019b) The electrical conductivity of the water during the study period ranged between 261 and 605  $\mu\text{S}/\text{cm}$ , with an average of 530  $\mu\text{S}/\text{cm}$ .

The majority of the catchment is part of a forest protection area, promoting biodiversity, is used as an ETH study site and thus minimally influenced by human interference (BAFU 2019). The catchment is mainly covered by a mixed deciduous forest, although a small area in the middle of the catchment is covered by mixed coniferous forest. There are two large and one smaller clearings with meadows, one of which (the meadow in the eastern part of the catchment) is also a big wetland/ spring area. The more western meadow (located below the sampling points) is a private cow pasture.

The stream network in the Diebis catchment is roughly 5.5 km long (figure 2.1). Two reaches were studied in this thesis: the one furthest to the west (flowing through point B), and the one furthest to the east (flowing through point C). The two come together in the lower part of the catchment (flowing through the outlet at point A; figures 2.1 and 2.2).



Figure 2.2 From left to right: Isco location A, B, and C. Location A is the one furthest downstream that was expected to show continuous flow most quickly. B is located on a reach in the western part of the catchment, location C is in the eastern part of the catchment. The reaches going through B and C ultimately run off through A. Next to the Iscos, the Keller loggers measuring the water level can be seen on all three pictures. The i::scans, which were only installed on locations A and C are installed on the same construction as the Keller loggers, as can be seen in the pictures to the left and to the right. The corresponding s::cans are located in boxes wrapped in black plastic bags to protect them from moisture.

The easternmost reach starts in a mixed deciduous forest, through which it runs for more than half of its length. It then flows into the eastern meadow (figure 2.3 left), through a spring area, and further downstream along the border of the meadow and the deciduous forest on the left looking downstream, effectively crossing the meadow. Afterwards, it flows through the forest, another wetland before merging with the other reach (figure 2.1).

The western part of the stream network is a bit of a special case, as the spring area of the upper left branch was affected by construction work after the first sampling campaign. Originally, it started at a wet meadow and was surrounded by blackberry bushes (figure 2.3 right). After the first event, most of the uppermost part of the streambed had been removed, and its surroundings had become a freshly turned, loamy wetland. This significantly affected the amount of sediment transported in the water during a rain event.

After the junction of the two source branches, the stream flows along a meadow, next to a mixed deciduous forest with more blackberry bushes. It crosses the lowest part of the meadow underground through a man-installed culvert into the lowest reach. The lowest investigated reach is located in a deciduous forest area and is incised into the soft, muddy soil. From there it flows towards the Reppisch.



Figure 2.3 The picture on the left shows the view looking from location C across the meadow towards the forest in the middle of the catchment. In the bottom left, the rain gauge can be seen. On the right, the more western meadow is depicted, before the upper stream reach was removed by construction.

Data collected for this thesis focused on the late fall/early winter period right after the summer 2018 drought and continued as the catchment rewetted. Unfortunately, there were few events in November, and sometimes snow instead of rain in December so that only five events could be sampled. A sixth event was sampled in May 2019 but because of a lack of data due to malfunctioning of the equipment (particularly the autosamplers), it was excluded from the analyses for this thesis.

### 3 MATERIAL AND METHODS

#### 3.1 HYDROMETRIC MEASUREMENTS

Pressure transducers (DCV-22 CTD, KELLER AG für Druckmesstechnik) were installed on three locations (A-C, see green diamonds in figure 2.1, and figure 3.1). The loggers recorded the pressure at a five-minute interval for most of the sampling season; there was a 22-day data gap in November due to work involving experiment setup. The pressure was corrected for atmospheric pressure, which was measured using another Keller logger installed close to the site A.

Precipitation was measured using a 0.2 mm resolution tipping bucket rain gauge (Odyssey Dataflow Systems Pty Limited). The gauge was installed in the middle of the meadow to avoid shielding from the forest canopy. Attached to the tipping bucket was a sequential rain sampler to collect rain water samples during the events at 5 mm intervals (Fischer et al 2017).

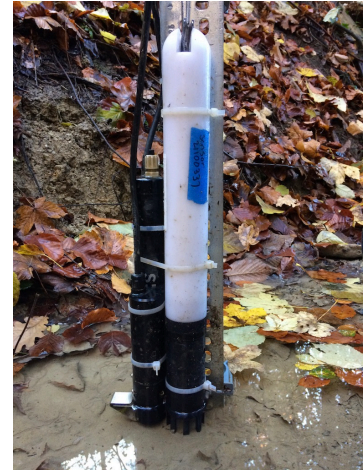


Figure 3.1 Keller logger (right) and i::scan probe (left) as seen on location A. The first is a pressure logger its data can be transformed into water level, the latter measures turbidity and UV254 reflectance.

#### 3.2 STREAM CHEMISTRY: CONTINUOUS MEASUREMENTS AND SAMPLING

Three Isco autosamplers (Isco 6712 Full-size Portable Sampler at location A, and Isco 2900 GLS Compact Samplers at locations B and C, Teledyne Isco, Inc.) (green diamonds on figure 2.1, barrel-like installations in figure 2.2) were installed on the same locations as the pressure transducers to obtain water samples during events. At two of these locations (A and C), i::scan loggers (con::lyte V5, i::scan Messtechnik GmbH) with i::scan probes (i::scan V1, i::scan Messtechnik GmbH) were installed (figure 3.1). These field spectrophotometers measured turbidity and UV254 reflectance at 20 minute intervals.

The automatic samplers were checked and programmed prior to the start of an event, usually two hours up to one day in advance, depending on the predicted onset of the precipitation (longer if the rain would start at night, or very early in the morning). The sampling interval of the autosampler with 22 (location B) to 24 (locations A and C) sample bottles was chosen to correspond with the predicted event duration to sample throughout the event. As one of the hypothesis investigated was to assess the extent of a first flush, more samples were taken at the beginning than at the end of an event. The i::scans were turned on and off along with the Iscos, except for events two, three, and four, which happened very close together so that the i::scans were let run over the entire period.

To determine the spatial variability in stream chemistry response, 29 single stage samplers SSS (red dots in figure 2.1, and figure 3.2) were installed along the different stream reaches throughout the catchment. They were designed to fill up at the onset of flow; an air bubble prevents further mixing during the event (Rick Assendelft 2018, personal communication). This way, a snap-shot sample of the first flush during an event could be taken.



Figure 3.2 Complete experiment setup on an SSS location. The sampler itself is installed on the bottom of the metal rod and covered by a plastic lid which allows for water circulation, while preventing the blockage of the bottle neck by bigger particles carried in the water.

The SSS were mounted on a metal rod, which had been planted into the ground in the slightly hollowed-out streambed. The samplers were installed at the height the water level would reach once the streambed was filled up and ready to continue flowing further downstream. On the same locations a second experiment was set up, monitoring the presence or absence of water, and whether or not there was flow (Rick Assendelft 2018, personal communication). As these apparatuses could easily clog, the sampler locations were regularly cleared out, and especially so before events, as to not obstruct flow into the SSS, and to enable clear measurements.

In order to assess the stream chemistry of baseflow, samples were taken intermittently to the rain events on six occasions and were analyzed along with the event streamwater samples. The first of these samples were taken before E1 on what little stream water was available, thus also offering a look into what the stream chemistry during the drought period was like.

### 3.3 LABORATORY ANALYSES OF THE SAMPLES

Directly after the events, the samples were emptied into two 50 ml plastic tubes. One was filled to the brim to allow for stable isotope analysis, as well as other hydrochemical parameter measurements, while the other, designated for a later analysis of carbon isotopic composition, was put in the freezer at  $-18^{\circ}\text{C}$ . Prior to analysis the samples were filtered using a  $0.45\ \mu\text{m}$  Simplepure™ syringe filter. Electric conductivity was measured in the lab for the unfiltered samples using an EC meter (Multi 3420 Digital Meter for Digital IDS Sensors, WTW GmbH).

The samples were analysed for the concentrations of dissolved organic carbon (DOC), cations, and anions at the Physics of Environmental Systems laboratory at ETH Zurich. The samples for the cation concentrations were acidified using  $50\ \mu\text{l}$  of  $50\ \text{mM HNO}_3$  solution to reduce precipitation and microbial activity, and were analysed on a mass spectrometer (ICP-MS 9700, Agilent Technologies). For the anion analyses an ion chromatograph (861 Advanced Compact IC, Metrohm) was used. Although all samples were analyzed for major and trace ion, only the results for chloride, nitrate, and phosphate (cations), and potassium and calcium (anions) are presented in this thesis. A total organic carbon analyzer (TOC-L Laboratory Total Organic Carbon Analyzers, Shimadzu) was used to determine the DOC concentrations.

The stable water isotope ratio measurements were done at the isotope laboratory of the Chairs of Hydrology at University of Freiburg, using a Cavity Ringdown Spectrometer (L2130-i (CRDS) Picarro Inc.), with an uncertainty of  $\pm 0.16\ \text{‰}$ . All water stable isotope data are presented using the delta notation relative to the Vienna Standard Mean Ocean Water (VSMOW) standard.

For a subset of the samples, the origin of the organic carbon dissolved in the water was determined. To this effect, samples from the beginning, the middle, and the ending of all events and locations were chosen and filled into individual tin-capsules to then be evaporated in the oven at  $60^{\circ}\text{C}$  for analysis of the carbon isotopic

composition. This analysis was done in house on a Combustion Module Cavity Ring-Down Spectroscopy (CM-CRDS) system, paired with an isotopic analyzer (G2131-i, Picarro Inc.), with a precision  $>0.3 \text{ ‰}$ . In order to enhance the signal of the samples with very little dissolved organic carbon, the re-filling and drying cycle was repeated eight times, with the last cycle done at  $80^{\circ}\text{C}$  to make sure the sample was completely dry. In addition to the analysis of the water samples, limestone samples taken from the field site were also analyzed, in order to determine the background signal from the calciferous bedrock. These samples were milled and analyzed similar to the water samples to determine their isotopic composition. All carbon isotope data are presented in delta notation relative to the Vienna Pee Dee Belemnite (VPDB) standard.

### 3.4 COMPUTER ANALYSES OF THE RESULTS

Although multiple hydrochemical parameters were analysed, nine main solutes were chosen to be studied more closely: electrical conductivity EC, stable water isotopic composition ( $\delta^{18}\text{O}$ ), dissolved organic carbon DOC, chloride-, nitrate-, phosphate-, potassium-, and calcium-ions, and UV254. This choice was made after looking at the data and deciding which parameters would be most interesting to explore because they were either the dominant solutes or changed most during the events.

Most of the data processing was done in Microsoft Excel (2016), and a small part of the analysis in R studio (R Core Team, 2019). The hysteresis classes for the relation between solute concentration and water level for each location and event, and the corresponding H values were obtained according to Zuecco et al., 2016, using their hysteresis tool. With it, the differences in hydrological responses during different events could be determined, which can be sorted into eight classes. Classes 1 to 4 represent an increase in solute concentration from the initial state, and thus more of a first flush, while classes 5 to 8 stand for a decrease from the initial state, therefore implying more of a dilution effect. Classes 1, 2, 5, and 6 move clockwise, 3, 4, 7, and 8 counter-clockwise. 1, 4, 5, and 8 behave in round loops, while 2, 3, 6, and 7 move in an 8-shaped loop. The H-values obtained in addition to the classes indicate the size of the loop: the further away from zero, the bigger the loop. H-values bigger than zero indicate a clockwise movement, values below zero one counter-clockwise. H-values around zero mean either there is no detectable hysteresis, the loop is a symmetrical 8-shape, or it's entirely too complex. As my data oftentimes wasn't behaving in a closing loop, meaning the hysteresis tool couldn't do its calculations, fixed water-levels in 0.05 increments were used.

To quantify the contribution of rainwater to the surface runoff, and thus the response of the catchment to precipitation, a two-component isotope-based hydrograph separation was performed using  $\delta^{18}\text{O}$  measurements from rain- and streamwater samples, following general practice.

All maps were done in QGIS (version 3.6, 2019).

## 4 RESULTS

### 4.1 GENERAL OVERVIEW AND EVENT DESCRIPTION

As stated before, over the course of the sampling season (October to December 2018) five rain events (E1 to E5) were sampled. In figure 4.1 the precipitation falling during the sampling period is shown, with the corresponding water levels measured on all three locations A, B, and C; the five events are indicated with arrows. The amount of rain that fell during until the end of the sampling season on the 31st of December amounts to 223.2 mm, and fell mostly during December 2018; the amount that had fallen by the end of E5 equals 143.4 mm (figure 4.2).

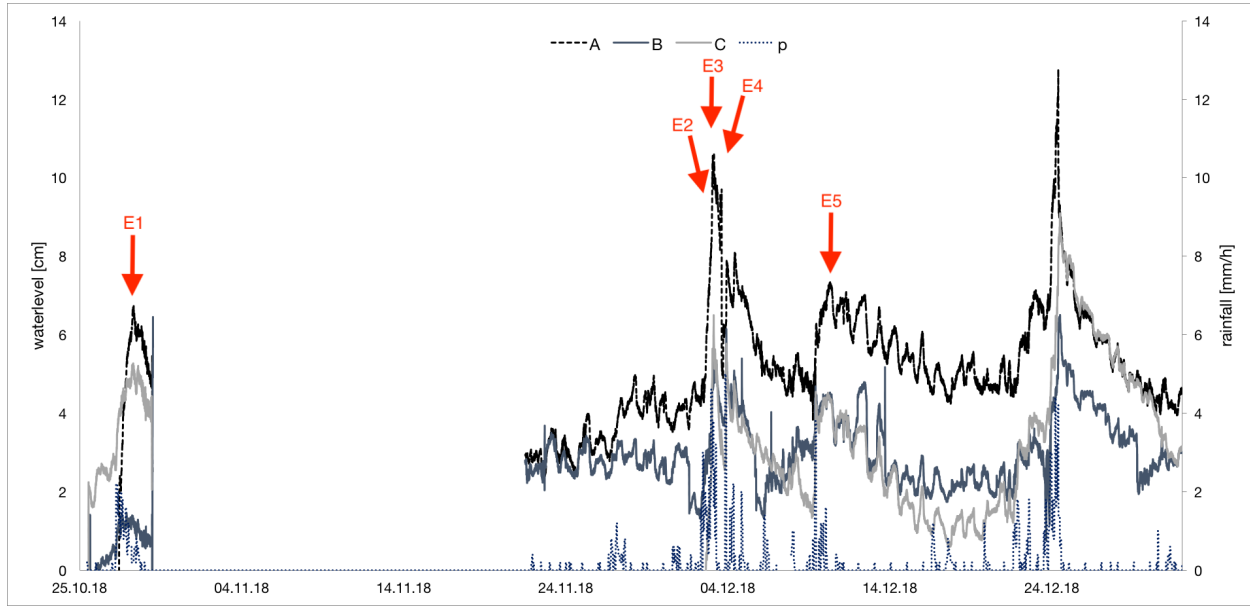


Figure 4.1 The rainfall over the whole sampling season, and the corresponding water levels for each location is shown. The events are indicated with red arrows.

The five events are of differing intensities (average precipitation intensity ranging from 0.3 mm/h during E5 to 1.9 mm/h in E3), differing event durations (E2 with 7.7 hours, and E5 with almost 24 hours length), as well as showing differences in the fraction of rainwater found in the surface runoff (average event-water fractions going from a very low 0.5% found in E5, to 10 to 20% of streamwater runoff being constituted by rain during E2 and E3 (figure 4.3). In table 1 all event characteristics can be found. As the rain gauge sampler was only installed after E1, an estimate in event-water fraction had to be made based on a comparison of the difference between the minimum and maximum value measured for  $\delta^{18}\text{O}$  found in all events. The measurements from location C were chosen for this as it's the location closest to the rain gauge. When running event-water fractions against the differences in  $\delta^{18}\text{O}$  a certain linearity appears visible, with the difference in  $\delta^{18}\text{O}$  being larger the higher the fraction of rain water in the streamflow (figure 4.4). This indicates a dilution effect.

Table 1 Main characteristics of the five events analyzed in this theses. The values for water level and event-water fraction were calculated over all three locations.

event	date – start	date – end	duration	max water-level	total precipitation	average precipitation intensity	max. hourly precipitation intensity	total precipitation in past 7 days	average event-water fraction $f_{e(\text{mean})}$	max. event-water fraction $f_{e(\text{max})}$
			<i>h</i>	<i>cm H<sub>2</sub>O</i>	<i>mm</i>	<i>mm/h</i>	<i>mm/h</i>	<i>mm</i>	<i>%</i>	<i>%</i>
E1	27.10.18 16:00	28.10.18 15:00	22.0	6.7	14.8	0.6	1.6	19	15.8*	–
E2	02.12.18 09:00	02.12.18 16:30	7.7	6.2	11.2	1.4	3.0	18	17.8	48.3
E3	02.12.18 17:00	03.12.18 08:20	19.0	10.6	30.8	1.9	4.6	30	8.0	27.0
E4	03.12.18 19:00	04.12.18 10:20	14.0	8.0	18.8	1.2	5.0	59	6.4	25.6
E5	09.12.18 10:00	10.12.18 07:30	23.8	7.3	6.4	0.3	1.6	83	0.5	14.7

\* estimated value

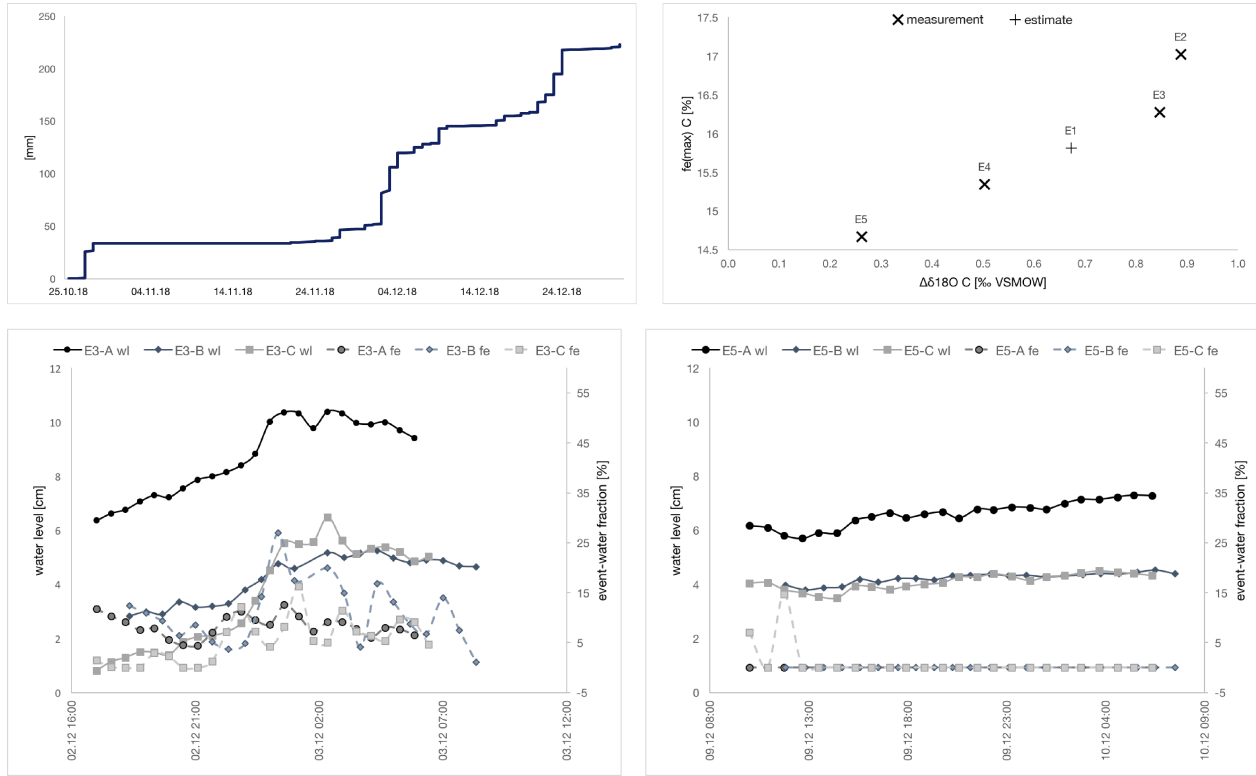


Figure 4.2 (top left) The cumulative precipitation that fell over the course of the sampling season. Most of the rain fell in December. Figure 4.3 (bottom) Water levels (drawn-through lines) and event-water fractions (dotted lines) found on all three locations during E3 and E5 after performing a hydrograph separation. E3 experienced much higher event-water fractions than E5, where they were mostly at zero. Figure 4.4 (top right) The relation between the maximum event-water fraction and the range in  $\delta^{18}O$  on location C, which allowed for an estimate of the event-water fraction of E1 which was otherwise unavailable.

To investigate the streamflow response, the max. water level was run against the amount of rainfall that had fallen during the event and the seven days prior to the event (figure 4.5). From this can be seen that E4 and E5, despite experiencing a lot of rain, had maximum water levels similar to E1 and E2 with much less rainfall. This hints at a difference in stream response, i.e. that the earlier events had a lot of rain water run off more or less directly as overland flow, while events later on in the sampling season already had a running stream that was less strongly influenced by rainfall. E3 shows the highest maximum water level with a medium amount of rain fall, indicating a strong dependence of streamflow on rainwater as runoff input.

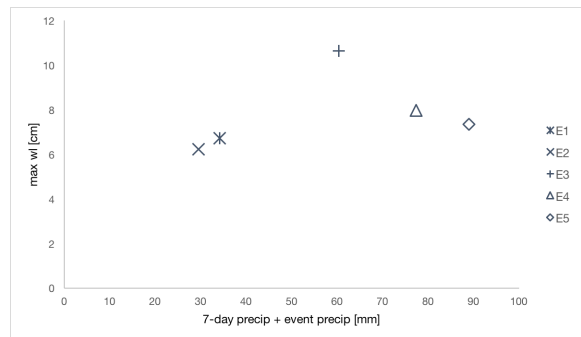


Figure 4.5 The relation between maximum water level and the total amount of rain over the past week + event precipitation, depicting streamflow response of every event.

These five events can be distinguished into three categories in accordance to their antecedent conditions and resulting flow connectivity. E1, as the first event after the drought period, had little antecedent soil moisture, low groundwater tables, and therefore low connectivity, resulting in little input of groundwater to surface runoff. E2, E3, and E4 all happened very close together (within 50 hours) and so reacted to similar antecedent conditions during the so called rewetting phase (Vazquez et al., 2014). These three events are considered as one



big intermediate event where soilwater is beginning to reconnect, and the groundwater tables are beginning to fill up again. In this thesis, E3 is discussed more thoroughly than E2 and E4, but shall stand for all three events unless mentioned otherwise. E5 was the first event where the groundwater had reconnected and added substantially to surface runoff, and is considered to have happened during the wet phase according to Vazquez et al. (2014), during which the basal hydrological conditions are re-established, making the stream resemble a perennial stream during the last event.

#### 4.2 BASEFLOW

The baseflow composition of water varied a little over the course of the sampling season, oftentimes similarly to the change visible from event to event.  $\delta^{18}\text{O}$  and calcium ion concentrations remained relatively constant from early October to mid-December, showing very similar value ranges as did the event samples (-10.11 to -9.59 ‰, coefficient of variation -0.02, and 47.6 to 80.3 mg/l, coefficient of variation 0.20, respectively). With values this high, calcium was the most abundant of all ions during baseflow, as well as later on during rain events. EC was higher than during rain events (on average 540 to 613  $\mu\text{S}/\text{cm}$ , coefficient of variation 0.13). The spatial distribution of EC found during one intermittent sampling campaign is shown in figure 4.6, where it can be seen that EC has a tendency to increase further downstream, and to change whenever multiple reaches come together.

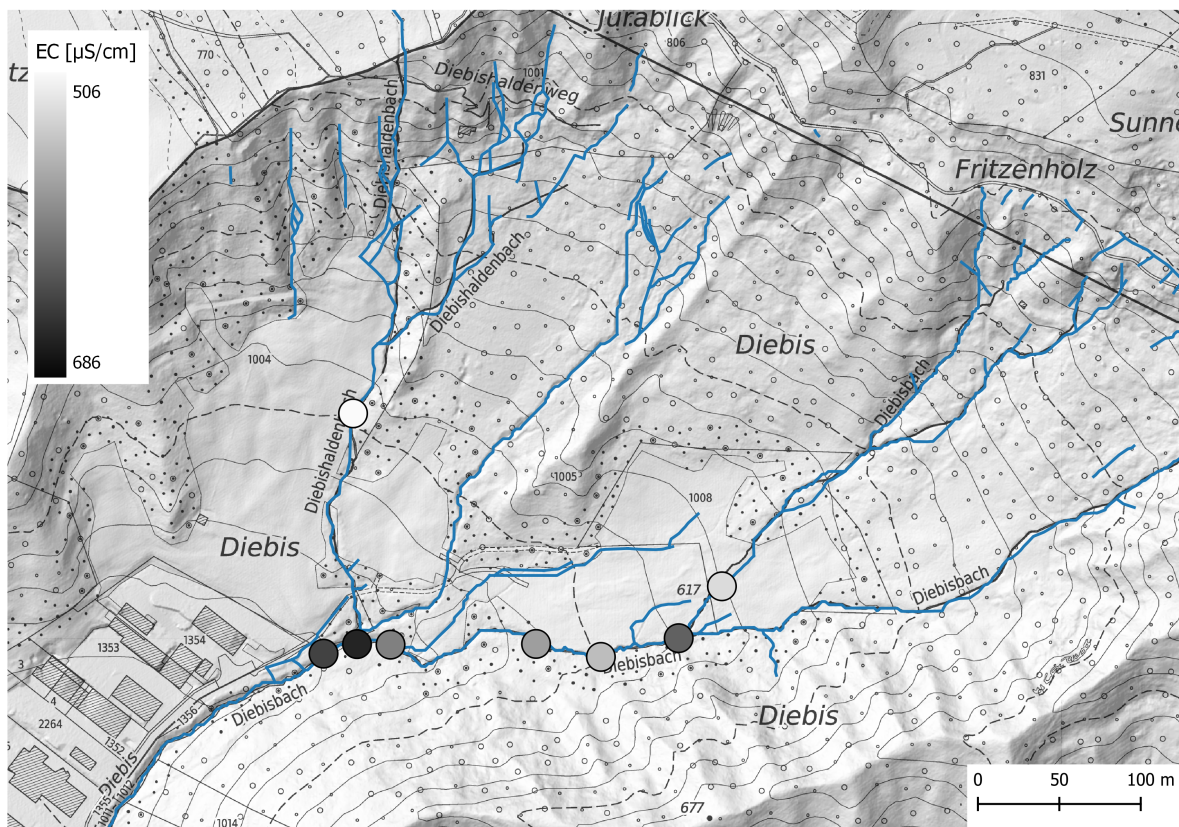


Figure 4.6 Map of the spatial distribution of electrical conductivity during baseflow conditions. EC increases moving further downstream.

The studied ion concentrations and DOC varied more strongly. DOC concentrations in baseflow was high in October and early November (53.4 to 74.7 mg/l, coefficient of variation = 0.1), thus actually being higher than the concentrations found later on in E1. The concentration then dropped drastically in mid-November and early December (3.3 to 6.4 mg/l, coefficient of variation = 0.2), to then rise again to concentrations higher than

what was found in the beginning of the sampling season (70.1 to 72.9 mg/l, coefficient of variation = 0.02), thus showing the same behavior as was found in the events (see subchapter 3.4 Dissolved Organic Carbon and table 2 solute-range).

Nitrate and sulfate ion concentrations showed the same behavioral pattern, though on a different scale (DOC ranged from 3.3 to 74.7 mg/l with a coefficient of variation of 0.6, nitrate from 0.015 to 5.2 mg/l with a coefficient of variation of 1.62, and sulfate from 5.0 to 67.8 mg/l with a coefficient of variation of 0.43). Potassium ion concentrations showed the opposite behavior, having low concentrations in October, early November, and again in mid-December, but higher concentrations from mid-November to mid-December (0.2 to 1.7 mg/l, coefficient of variation = 0.43). Chloride ion concentrations steadily increased over the course of the season (from an average of 2.7 mg/l in the beginning of the sampling season, to a mean of 4.5 mg/l in mid-December).

Nitrate showed the largest coefficient of variation during baseflow, and so it did too during the rain events, with a coefficient of 0.82 during E3 on location B. The smallest coefficients of variation were found for DOC, chloride, and sulfate, all during E5 on location C (coefficient of variation = 0.02). Over all solutes, E1 showed the largest coefficients of variation on average, while E5 had the smallest.

Table 2 Ranges in solute concentration for each event and location, and their corresponding coefficient of variation (CV).

event	solute location	$\delta^{18}\text{O}$		EC		DOC		$\text{Cl}^-$		$\text{NO}_3^-$		$\text{SO}_4^{2-}$		$\text{K}^+$		$\text{Ca}^{2+}$		UV254 Abs/m	
		%	CV	$\mu\text{S/cm}$	CV	mg/l	CV	mg/l	CV	mg/l	CV	mg/l	CV	mg/l	CV	mg/l	CV		
E1	A	-10.44 – -9.71	-0.02	455 – 529	0.04	28.1 – 54.7	0.21	0.9 – 3.1	0.38	0.44	0.8 – 5.9	0.44	6.2 – 24.5	0.32	0.5 – 2.5	0.44	31.5 – 68.7	0.20	*
	B	-11.21 – -10.30	-0.02	415 – 498	0.05	22.5 – 57.4	0.25	0.5 – 2.9	0.37	0.38	0.4 – 2.2	0.38	1.8 – 7.9	0.36	0.3 – 1.7	0.35	16.8 – 64.4	0.30	**
	C	-10.24 – -9.57	-0.01	462 – 577	0.05	22.2 – 54.8	0.19	1.3 – 5.0	0.32	0.29	1.2 – 4.2	0.29	4.9 – 21.2	0.34	0.5 – 1.7	0.33	28.1 – 61.7	0.20	*
E2	A	-10.93 – -10.04	-0.03	526 – 605	0.05	3.9 – 6.1	0.12	2.0 – 2.4	0.05	0.78	0.0 – 0.5	0.78	8.6 – 24.7	0.31	0.9 – 2.7	0.29	58.7 – 66.0	0.03	9.0 – 77.0
	B	-12.69 – -11.17	-0.03	377 – 481	0.06	4.5 – 6.5	0.11	2.7 – 2.9	0.02	0.07	0.5 – 0.6	0.07	2.2 – 4.4	0.20	2.1 – 2.7	0.07	42.6 – 49.1	0.04	**
E3	A	-10.46 – -10.11	-0.01	479 – 546	0.05	5.4 – 6.2	0.04	2.5 – 3.2	0.08	0.23	0.6 – 1.5	0.23	5.6 – 14.9	0.35	1.4 – 2.8	0.19	57.5 – 66.4	0.04	15.4 – 122.0
	B	-11.28 – -10.28	-0.02	396 – 517	0.07	4.5 – 8.0	0.16	2.6 – 3.5	0.09	0.82	0.4 – 2.4	0.82	2.9 – 7.2	0.26	1.6 – 2.4	0.10	42.0 – 59.2	0.08	**
	C	-10.67 – -9.83	-0.02	447 – 579	0.08	5.0 – 5.8	0.04	4.8 – 5.7	0.05	0.48	0.6 – 4.2	0.48	5.8 – 12.2	0.23	1.0 – 2.7	0.31	57.4 – 75.8	0.08	12.1 – 14.5
E4	A	-10.24 – -9.94	-0.01	261 – 559	0.13	3.1 – 5.3	0.10	1.1 – 2.7	0.14	0.15	1.9 – 5.2	0.15	8.3 – 22.2	0.15	0.5 – 1.3	0.19	26.7 – 51.9	0.15	*
	B	-10.58 – -9.75	-0.02	294 – 546	0.12	3.0 – 6.7	0.12	1.8 – 3.3	0.12	0.14	1.3 – 3.0	0.14	6.1 – 12.3	0.16	0.6 – 1.6	0.14	25.2 – 42.3	0.10	**
	C	-10.28 – -9.78	-0.01	434 – 577	0.05	4.1 – 4.8 <sup>◇</sup>	0.04	*	*	*	*	*	*	*	0.4 – 1.1	0.22	56.2 – 94.9	0.15	*
E5	A	-9.92 – -9.62	-0.01	495 – 587	0.04	69.0 – 82.7	0.05	3.0 – 7.9	0.37	0.05	2.6 – 3.2	0.05	19.1 – 24.2	0.05	0.6 – 0.8	0.07	41.5 – 58.6	0.09	*
	B	-10.09 – -9.74	-0.01	431 – 535	0.04	59.6 – 88.0	0.09	2.9 – 7.6	0.31	0.11	2.4 – 3.9	0.11	8.9 – 19.3	0.20	1.0 – 1.4	0.07	30.9 – 44.8	0.08	**
	C	-9.80 – -9.54	-0.01	428 – 640	0.07	69.0 – 77.1	0.02	7.7 – 8.2	0.02	0.05	3.1 – 3.8	0.05	19.1 – 20.3	0.02	0.5 – 0.7	0.12	46.1 – 59.8	0.09	5.9 – 174.2

\* no or too little data

\*\* no sensor at location B

◇ outlier value (55.5 mg/l) removed

#### 4.3 ISOTOPIC COMPOSITION OF STREAMWATER AND EVENT WATER FRACTIONS

The isotopic composition of streamwater generally varied little throughout the rainfall event (coefficient of variation ranged between -0.03 for location B during event E2 to -0.01 for location A during event E5). The isotopic composition of streamwater at location A and C was similar for all events but usually more depleted and more variable for location B (see table 2). This pattern was most pronounced during the first event (E1; figures 4.7, 4.8, and 4.9). During E3, stream water became more depleted during the event, reflecting the depleted signature of the rain water, suggesting a significant contribution of rain water during this event (see table 1 event characteristics). The spatial and temporal variation in the isotopic composition of the stream water were least pronounced during the fifth event (E5) because the isotopic composition of the rainwater was only slightly more enriched than that of the streamflow. For all events and locations, there was limited hysteresis between the isotopic composition of stream water and the water level (the H-values are close to zero; table 3).

Table 3 Hysteresis classes to show the relation between solute concentrations and water level for each location and event, and the corresponding H-values, according to Zuecco et al. (2016).

event	solute location	$\delta^{18}\text{O}$		EC		DOC		Cl <sup>-</sup>		NO <sup>3-</sup>		SO <sub>4</sub> <sup>2-</sup>		K <sup>+</sup>		Ca <sup>2+</sup>	
		h	class	h	class	h	class	h	class	h	class	h	class	h	class	h	class
E1	A	-0.57	7	-30.0	3	-23.48	3	-26.63	3	-28.19	3	-28.64	3	-7.31	3	-9.34	3
	B	2.92	6	8.7	6	-28.05	3	-21.33	3	-20.73	3	-18.64	3	-21.67	3	-30.03	3
	C	4.10	2	-6.8	3	-21.92	3	-16.81	7	-2.49	7	-16.99	3	-11.28	7	-25.48	3
E2	A	3.85	6	17.9	6	-13.28	3	-17.35	3	-24.71	3	7.21	6	-15.53	3	7.53	6
	B	12.95	6	12.4	6	4.68	2	-2.30	3	-29.72	3	-10.06	3	5.66	6	17.36	6
E3	A	-0.01	3	18.4	6	-6.79	3	-27.50	3	-27.28	3	11.55	2	6.75	2	2.75	6
	B	3.90	6	8.7	6	-7.46	3	-11.30	3	-0.30	3	-22.75	3	6.87	2	-4.43	7
	C	5.11	6	19.3	6	6.43	6	-2.10	7	23.62	6	17.51	6	26.31	6	17.19	6
E4	A	0.71	2	0.0	0	-3.75	7	-1.84	7	-0.63	7	4.62	6	0.99	2	-10.36	7
	B	-3.26	3	3.6	6	-3.26	3	4.60	6	3.25	6	6.30	6	-4.22	3	1.76	2
	C	12.54	6	10.9	6	-20.64	3	*	*	*	*	*	*	-4.83	3	19.37	6
E5	A	2.00	6	-9.8	7	7.67	6	29.85	2	16.87	2	-25.40	7	18.34	6	-14.70	7
	B	23.16	6	-12.7	7	16.92	2	0.29	6	2.91	6	-1.43	3	7.62	6	-2.87	7
	C	8.23	6	-3.1	7	0.37	2	-3.71	3	-6.76	7	-11.78	7	13.79	6	8.27	2

\* no data on these solutes

#### 4.4 ELECTRICAL CONDUCTIVITY (EC)

The variation in EC was relatively high during the first event (E1; coefficient of variation ranging between 0.04 at location A to 0.05 at locations B and C), rose further in later events (e.g. coefficient of variation during E3 ranged between 0.05 (location A) to 0.08 (location C)), and finally dropped back for E5 (coefficient of variation ranging between 0.04 (locations A and B) and 0.07) (figure 4.12). There was no clear decrease in EC during events E1 and E5, while there was a clear decrease in EC during peak streamflow (high water level) during E2 and E3 (i.e., during the period with high event-water fractions; see table 1 event characteristics, and figure 4.11), suggesting dilution of the streamwater by precipitation. For all three locations the EC increased in the beginning of E1, suggesting that material that had been accumulating prior to this event was washed out at the onset of flow, but during all following events it decreased, indicating dilution (figure 4.10). Although the temporal variation in EC was similar for all three locations, the fluctuations at site B were larger than at A and C, in line with the larger variations in  $\delta^{18}\text{O}$ .

#### 4.5 DISSOLVED ORGANIC CARBON (DOC)

The fluctuations in dissolved organic carbon (DOC) concentrations were also largest during the first event and decreased in later events. However, unlike the variations in EC, which were relatively small, the concentrations of DOC differed greatly for the different events (see table 2, and figure 4.15). During E1, the DOC concentrations were high for all three locations, with location B having the highest values. The DOC concentrations increased with increasing water levels, indicating flushing of carbon. For events E2 and E3, the concentrations of DOC dropped drastically ( $<10$  mg/l) for all three locations (figures 4.13 and 4.14). This can be related to the very high event water fractions during causing dilution (tables 1 and 2). It is interesting to note that, even though the concentrations of DOC were very low, a first-flush-behaviour could still be seen at locations A and B, while on location C the concentrations decreased during the rising limb. During E5 the highest concentrations of DOC were observed throughout the event, especially on location B. The hysteresis between DOC concentrations and water level for this event suggest that for locations B and C, there was an increase in DOC in the water at the beginning of the event, while for location A the increase occurred later (see table 3).

#### 4.6 ANIONS – CHLORIDE, NITRATE, AND SULFATE

Over all events, chloride showed strong temporal variation with the lowest overall range during E1, but quieted down a lot by event 2, from then on only behaving in small fluctuations (figure 4.16). Similar concentrations as were found for E1 were seen during E2, E3 and E4 (except for higher concentrations on location C during E3) (see table 2). The concentrations were very stable in E5, with almost no fluctuations, and concentrations very similar to prior events, except, again, for much higher values found on location C (figure 4.18). Nitrate, too, showed lots of (noisy) change in concentrations during the first event, with a corresponding increase in water level visible but not too high (max. of 3 cm) (figure 4.17). Overall, nitrate behaved very similarly to chloride, except for showing a wider range during E1, and lower concentrations during events E2 to E4. Locations A and B during E5 strongly resembled what was seen for chloride, concentrations from location C, however, were, with concentrations similar to concentrations of locations A and B, much lower. Concentrations found on locations A and B for E3 still showed some change in concentration during the event, but far less pronounced than during E1, while location C showed the greatest range in concentrations of all five events (table 2 solute range, and figure 4.18). An increase in concentrations was seen with increasing water level (table 3), whereby the rise in water level was about twice as high as in E1 (max. 6 cm) (table 1). Sulfate concentrations ranged the widest of all three anion concentrations during E1, while also showing some of the highest values. While E2 and E4 showed almost equally high and erratically behaving concentrations as E1, during E3, the range was lower and concentrations overall less high, with a slight increase in the amounts of sulfate dissolved in the water

in the beginning of the event on locations A and B, while location C experienced a decrease in sulfate concentrations. The highest overall concentrations were found during E5, which was also the most stable of all events. Interestingly, the three different locations for once showed no overlap, with A having the highest concentrations, followed by C, both having higher amounts than the ones found on location B (figures 4.16, and 4.18).

#### 4.7 CATIONS – CALCIUM AND POTASSIUM

In a comparison of the two cations considered in this thesis the first thing to be noted is how much higher the concentrations of calcium ions are than what is found in potassium concentrations. While potassium ion concentrations mostly ranged around mean values of about 1 mg/l, calcium ions were abounded with mean amounts of almost 50 mg/l (see table 2). The calcium and potassium concentrations fluctuated quite strongly during almost all events, but mostly so during E1 (figure 4.19). During E1, concentrations of both solutes vary largely, with especially high peaks at the beginning of the event. This is also reflected in the hysteresis, indicating a (small) first flush (except, again, for location C for  $K^+$  (table 3, and figure 4.20)). For the intermittent events (e.g. E3), there was a first increase in the concentrations of  $K^+$  for locations A and B, with a corresponding decrease in  $Ca^{2+}$  concentrations at about the same time. However, at location C the  $K^+$  concentrations resembled the changes in  $Ca^{2+}$  concentrations. During E5, the dilution pattern for the two cations was similar, showing only a belated increase in concentrations, if any. The concentrations of  $Ca^{2+}$ , though fluctuating, were higher in the beginning. The highest  $K^+$  concentrations were found on location B, which was also the location with the lowest  $Ca^{2+}$  concentrations during the event (figure 4.21).

#### 4.8 ORIGIN OF DISSOLVED CARBON

$\Delta^{13}C$  was measured on filtered, but un-acidified water samples, which means that the  $\delta^{13}C$  value is a mixed signal of DOC and DIC found in the stream water. In addition to the measurements made on streamwater samples, the  $\delta^{13}C$  ratio of limestone found in the catchment was also measured to allow for statements about the ratio of DOC/DIC in the samples. It was found that, overall, (1) with more organic carbon dissolved in the water the  $\delta^{13}C$  values are less depleted and thus closer to the  $\delta^{13}C$  ratios found for the rock samples, and (2) with high DOC concentrations, location B tends to have the least negative  $\delta^{13}C$  ratios, followed by A, and finally C showing the most depleted values, while with low DOC concentrations the  $\delta^{13}C$  values gotten on locations A and B are very similar, and tend to be much less negative than the values found on location C (figure 4.22). All streamwater values, except for the first value gotten on location A during E4, ranged between -5 and -12 ‰ (E4.A.1 = -15.13 ‰), and the rock samples having an averaged  $\delta^{13}C$  ratio of -4.83 ‰. The values found during E1 were in between E3 and E5 both in terms of DOC concentrations, as well as  $\delta^{13}C$  ratios (figure 4.22), and were found to become less depleted over the course of the event on all locations, while DOC concentrations fluctuated quite strongly (figure 4.23). During E3, the  $\delta^{13}C$  ratios were much more stable than during E1. The least amount of DOC was found during this event (and also during E2 and E4), which coincides with the most negative  $\delta^{13}C$  ratios. In E5,  $\delta^{13}C$  values closest to what was found for the rock samples were seen. The streamwater on location B showed  $\delta^{13}C$  values similar to the rock samples' for the first half of the event, but got more depleted towards the end. DOC, on the other hand, became less until the last third of the event, where it increased again in a late flush. The streamwater samples from location A became steadily less depleted in  $^{13}C$  over the course of the event, while DOC concentrations varied only little (coefficient of variation = 0.05).  $\Delta^{13}C$  on location C varied the least, remaining constantly lowest of the three locations. Location C also had the least varying DOC concentrations of this event.

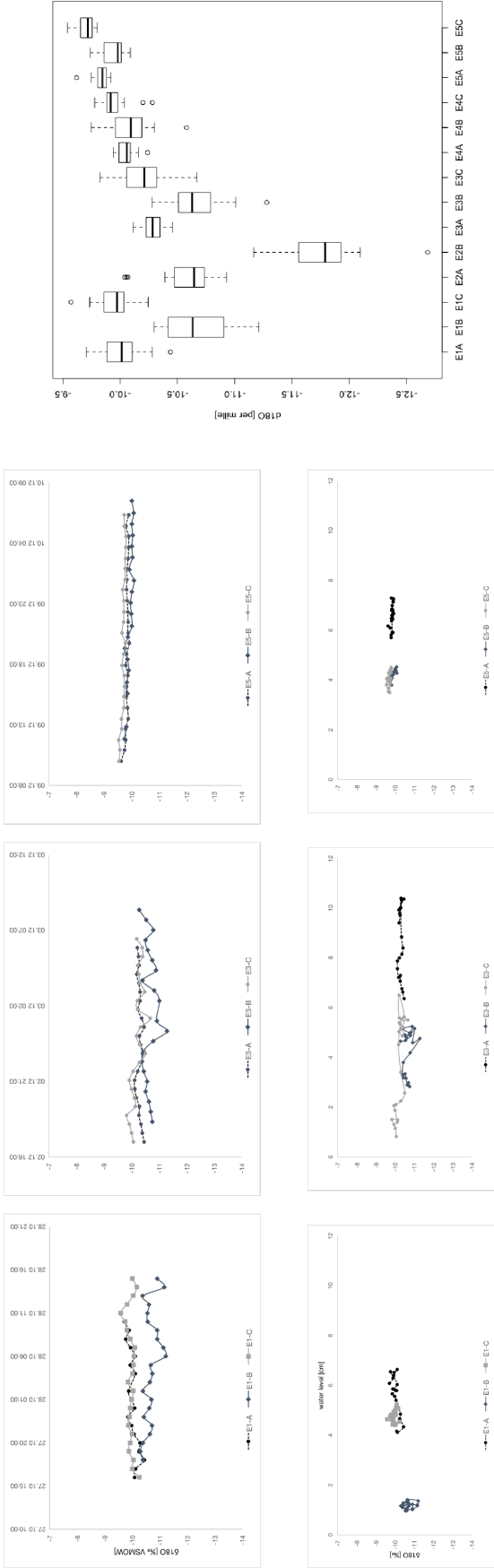


Figure 4.7 (top) Timeseries of the isotopic composition development during E1, E3, and E5.  
 Figure 4.8 (bottom) Relation between isotopic composition and water level during E1, E3, and E5.  
 Figure 4.9 (right) Boxplots depicting both temporal and spatial variation of isotopic composition during all events, on all locations.

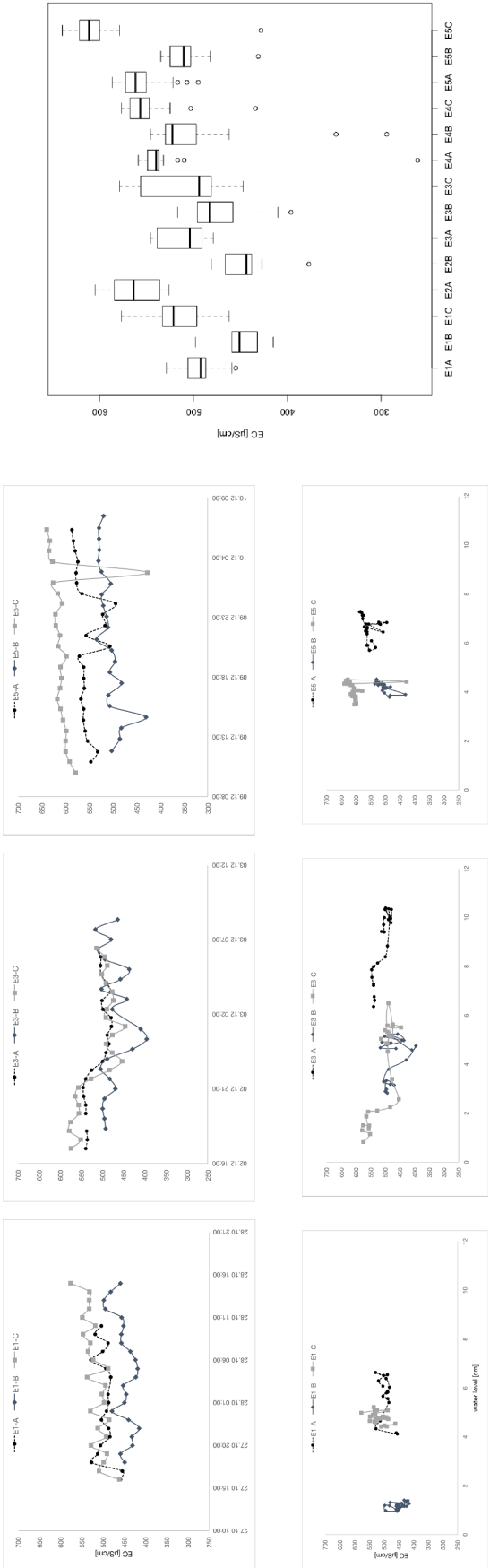


Figure 4.10 (top) Timeseries of EC during E1, E3, and E5.  
 Figure 4.11 (bottom) Relation between EC and water level during E1, E3, and E5.  
 Figure 4.12 (right) Boxplots depicting the temporal and spatial variation of EC during all events, on all locations.



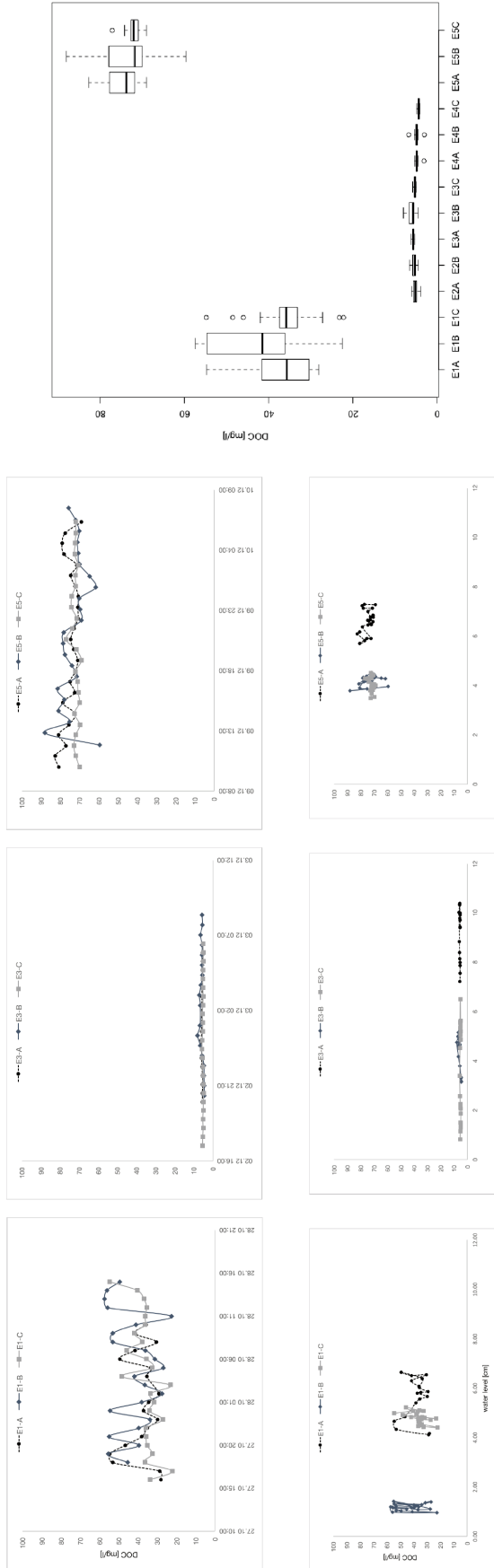


Figure 4.13 (top) Timeseries of DOC during E1, E3, and E5.

Figure 4.14 (bottom) Relation between DOC and water level during E1, E3, and E5.

Figure 4.15 Boxplots depicting temporal and spatial variation of DOC during all events, on all locations.

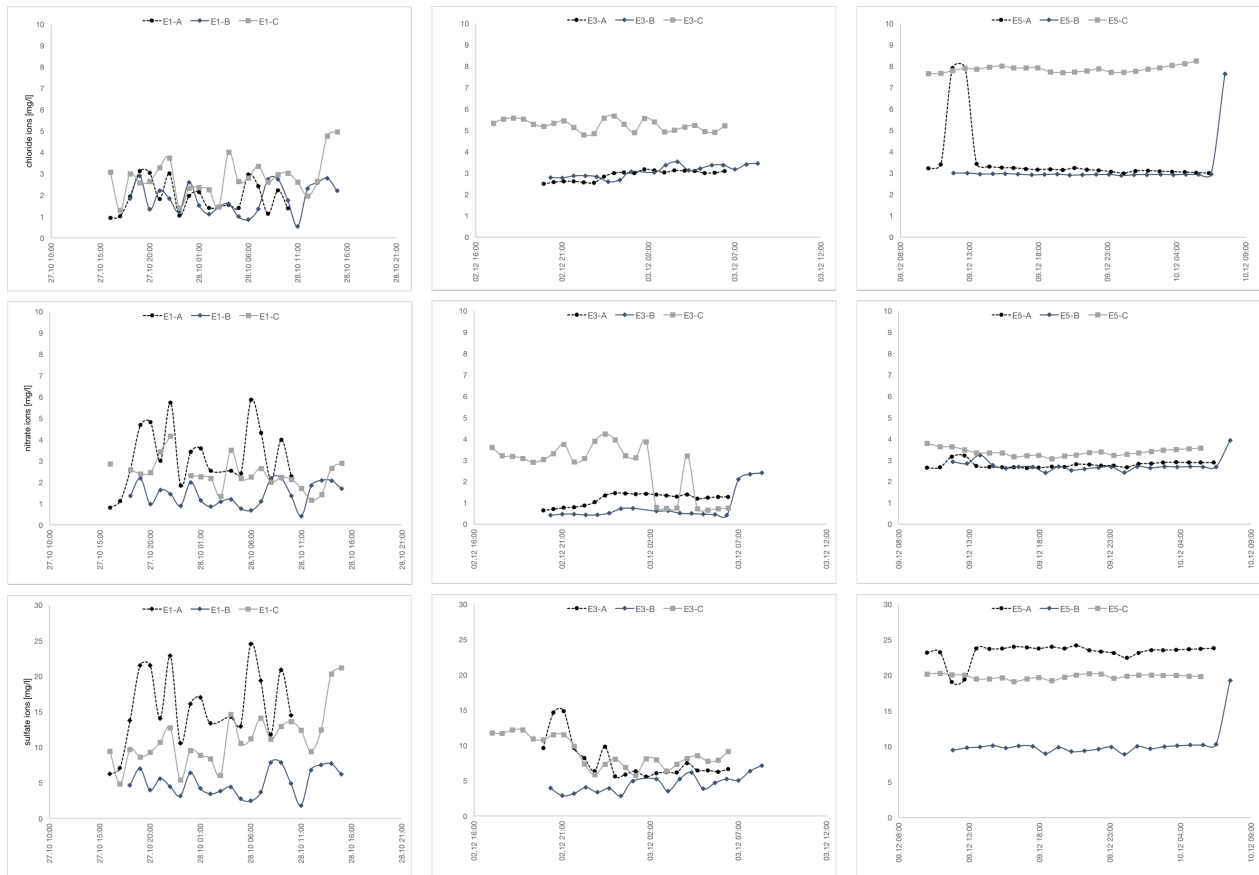


Figure 4.16 Timeseries of all anions during E1, E3, and E5.

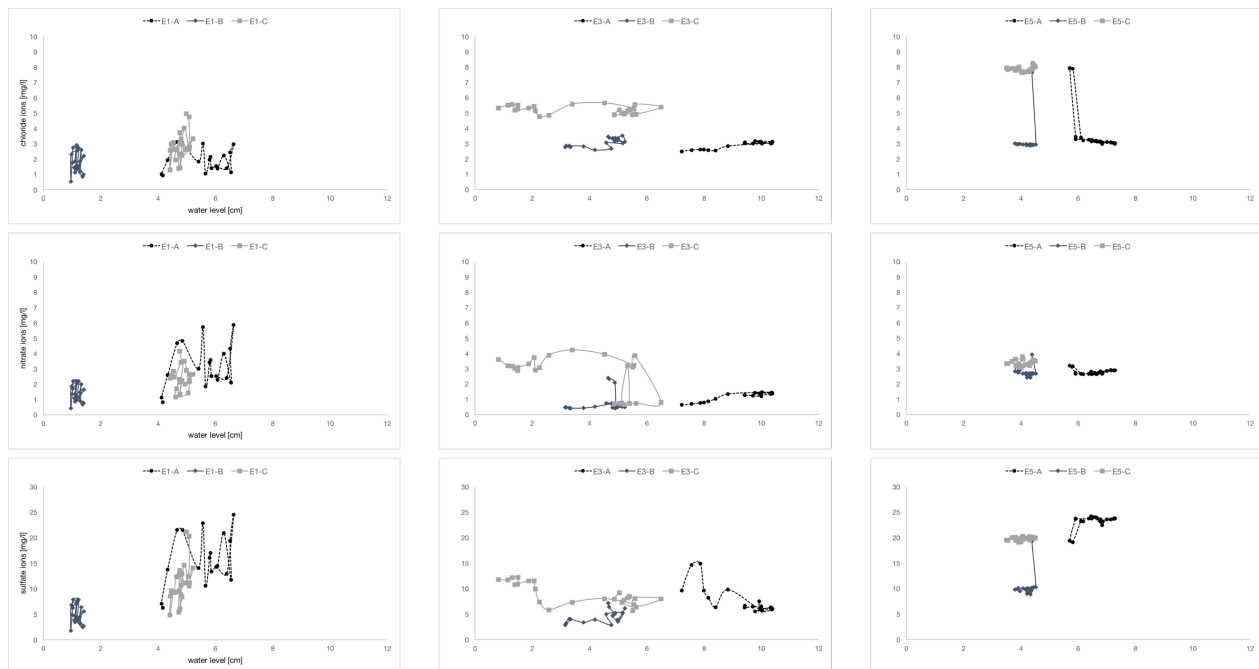


Figure 4.17 Relation between the anion concentrations and water levels during E1, E3, and E5.

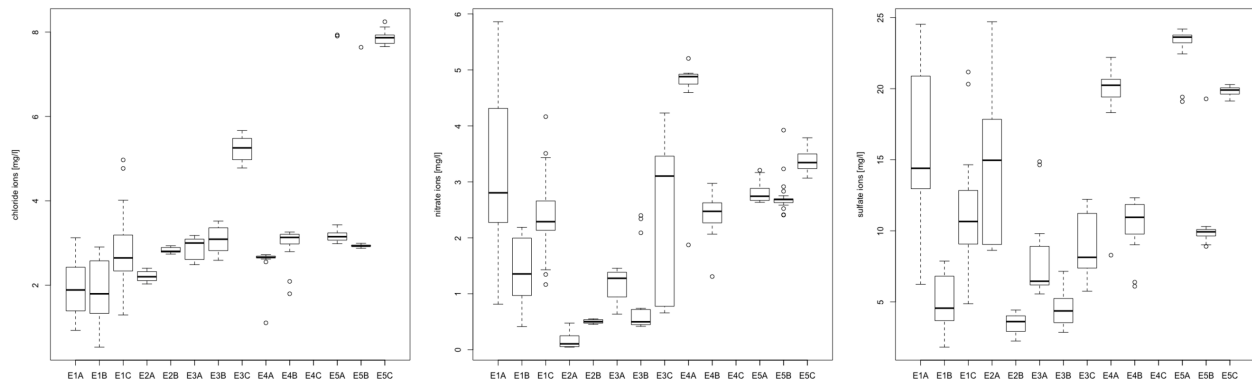


Figure 4.18 Boxplots depicting the temporal and spatial variations of the three anions during all events, on all locations.

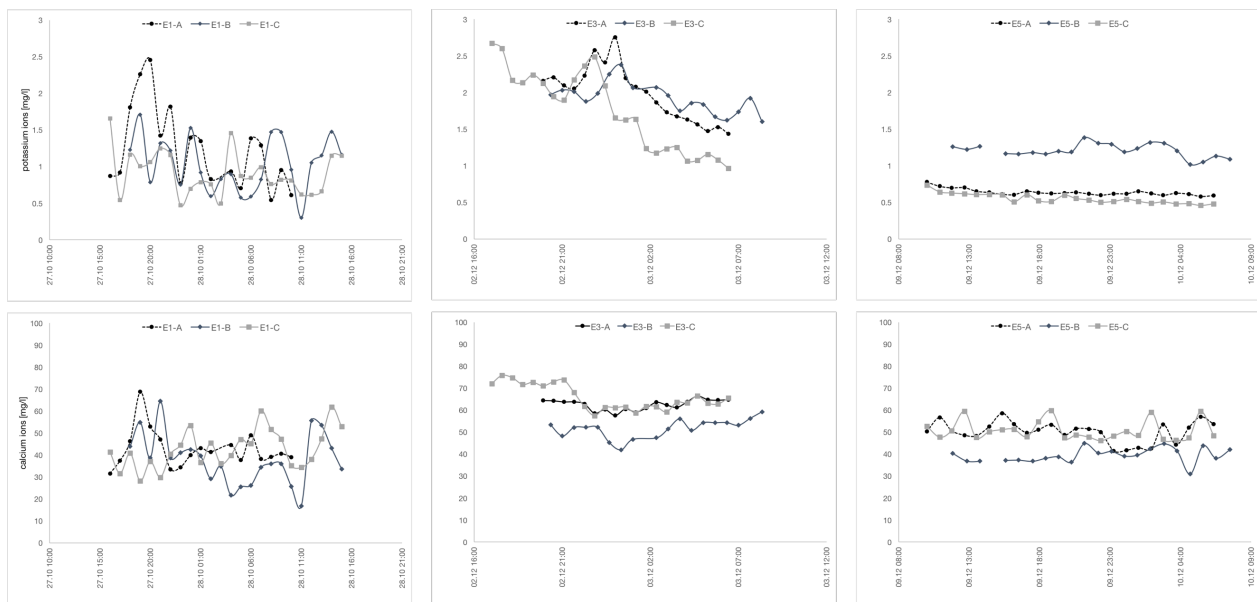


Figure 4.19 Timeseries of the two cations during E1, E3, and E5.

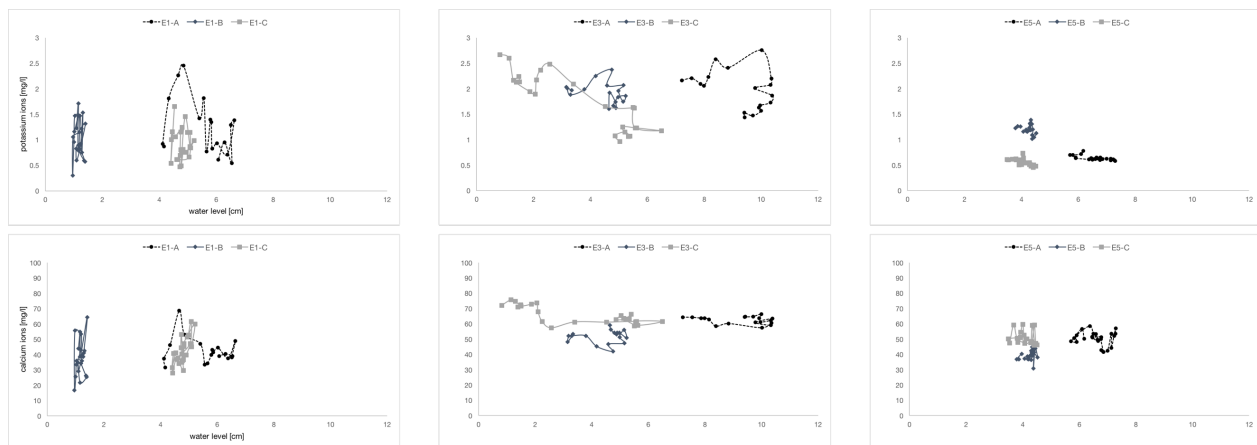


Figure 4.20 Relation between the concentrations of the two cations during E1, E3, and E5.

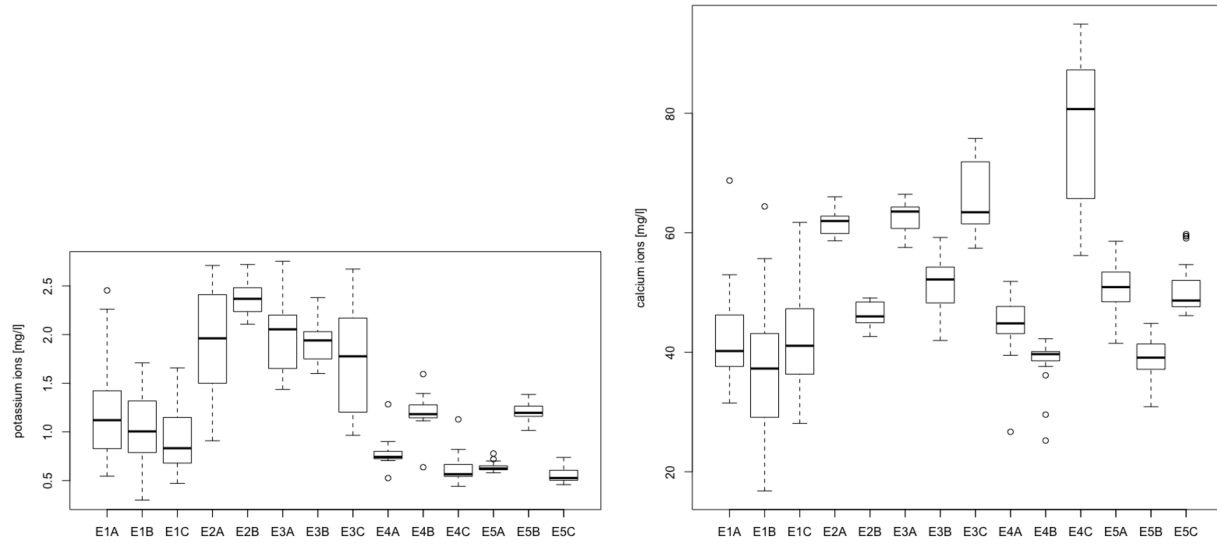


Figure 4.20 Boxplots depicting the temporal and spatial variation found in the two cations during all events, on all locations.

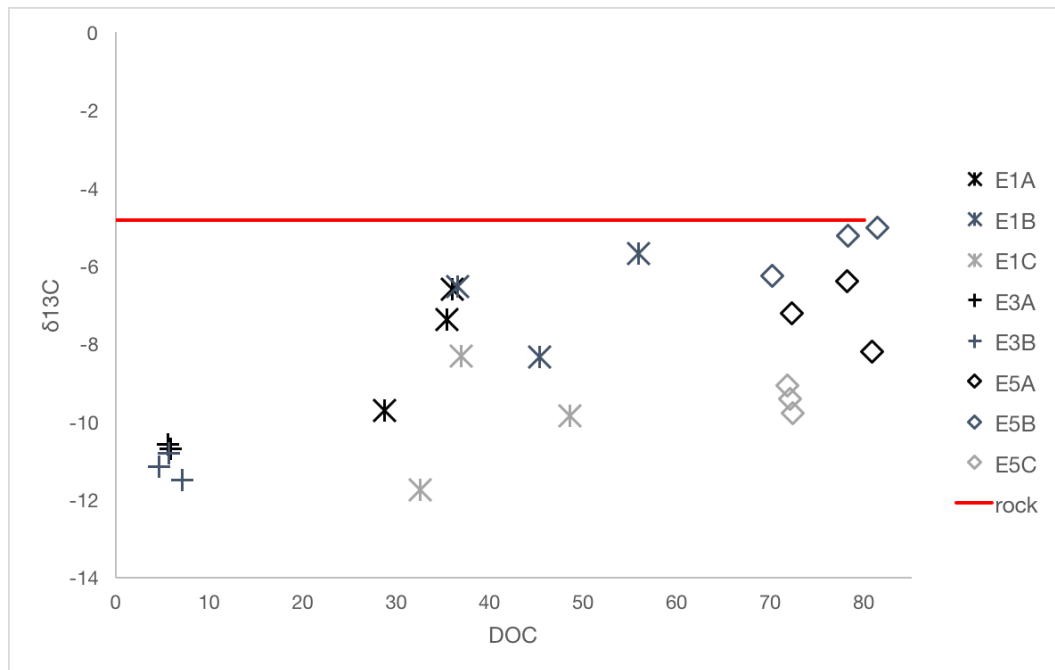


Figure 4.22 Relation between DOC and carbon isotopic composition, which can be use to deduce DOC/DIC ratios.

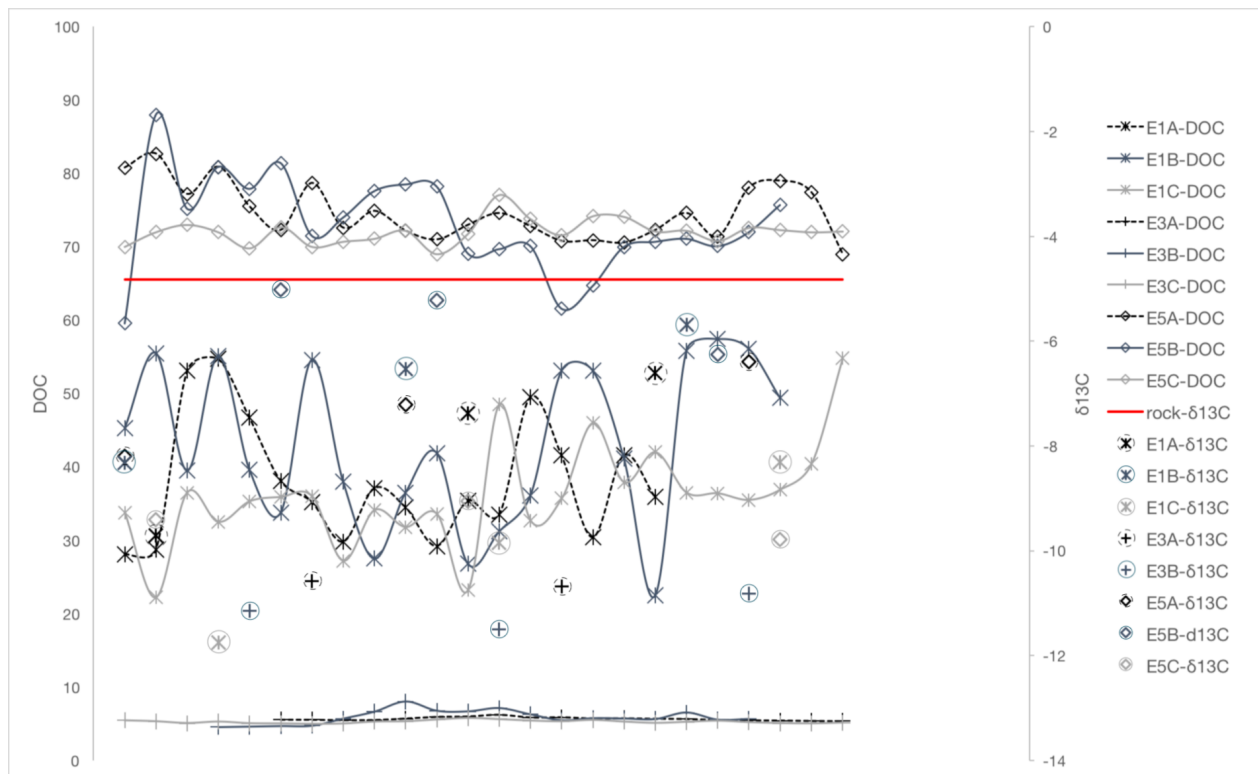


Figure 4.23 Temporal evolution of DOC and carbon isotopic composition.

#### 4.9 SINGLE STAGE SAMPLERS (SSS)

As it happened, the entirety of the intermittent stream network was never activated during the sampling season. Because of this, during most of the events, only the same single stage samplers, if any, were actually filled. As only two samples, which were right next to each other, don't offer a lot of insight into spatial variation in the catchment, events with only these two single stage measurements will not be discussed further in this thesis. Only during E2 six samplers in total filled up, which are presented in figure 4.24 E2-SSS-maps. In addition to the SSS measurements, the concentrations found in one of the first samples taken from locations A and B are shown for a more complete overview of spatial variability (no measurements were taken on location C during this event). The map depicting  $\delta^{18}\text{O}$  showed that samples taken further upstream were different from the samples taken downstream. Water became less depleted when moving through the catchment, except for the stream furthest to the right (looking downstream), where the sample taken on Isco location B is a little more depleted in  $^{18}\text{O}$  than the sample taken further upstream. EC showed a similar pattern, as electrical conductivity was generally higher further downstream and in the eastern part of the catchment. DOC concentrations show a similar pattern in the three downstream SSS, but the opposite for the SSS highest up in the catchment, the one right above location C, as well as for the first Isco measurement on location A. The concentrations measured in the three anions partly follows what is seen for EC in that the measurements taken at the three SSS locations above Isco location A are all also relatively high, as are the samples from the SSS in the middle part of the catchment. The measurements taken from locations A differ from what was found for EC as they are very low. The values of chloride and nitrate concentrations taken on the SSS location highest up in the catchment also differs from the pattern found for EC as they are quite high. No cations were measured in these samples.

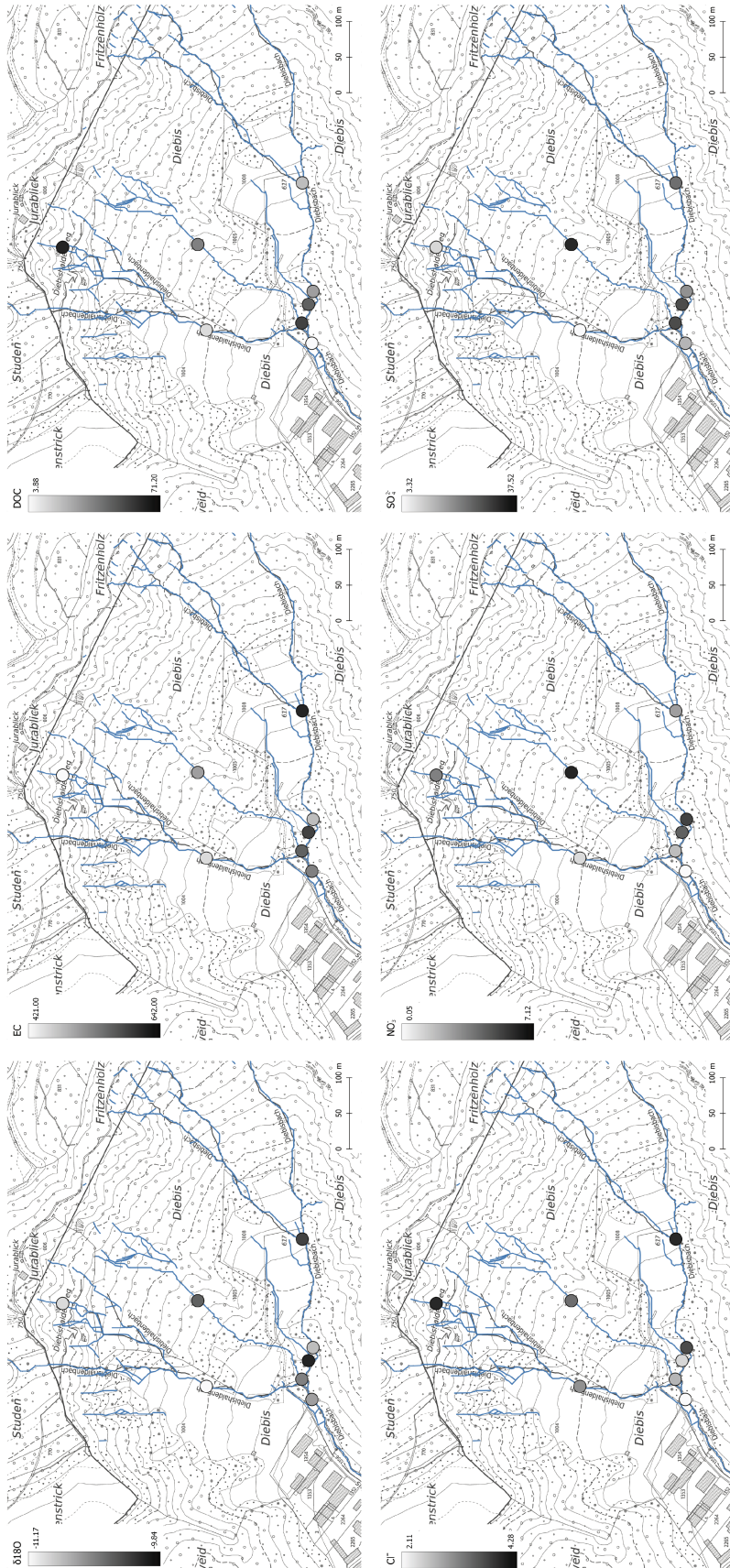


Figure 4.24 Results of the SSS samples taken during E2.

#### 4.10 I:SCAN MEASUREMENTS – TSS<sub>EQ</sub> AND UV254

Due to varying factors (cold temperatures, relatively old batteries, wrong connection of probes, etc.) the two i:scan probes weren't turned on during the entirety of all events, leading to an incomplete data set. In addition, further measurements were unusable as the parameters were out of measurement capabilities, ultimately resulting in a data set with many missing values. It is thus that these measurements are excluded from further analysis, as they do not contribute greatly to a better understanding of the remaining data. The only thing that can be stated in relation to the UV254 measurements is that, most of the time, they correlated well with the DOC concentrations found in the streamwater, i.e. high reflectance in this spectrum when there were high concentrations of organic carbon dissolved in the water (table 2).

## 5 DISCUSSION

Streamwater samples were taken during five events over the course of the re-wetting period in late fall/early winter 2018, and subsequently analyzed for different hydrochemical parameters. Antecedent moisture conditions have a strong impact on how a catchment responds to rainfall in terms of hydrology and biogeochemistry (Bernal et al., 2019). To take this into account, E1 represents the first rainfall after a long drought period on an intermittent stream, E2, E3, and E4 the re-wetting of the catchment, and E5 the re-connection of groundwater to the stream system, making the stream more perennial-like. With these measurements the stream chemistry change over the course of the rainfall events, how these changes vary within the catchment, and how they change over the course of the entire sampling period was studied.

### 5.1 STREAMWATER CHEMISTRY CHANGES WITH RAIN

While change in streamwater chemistry could definitely be seen in all solutes, it wasn't equally pronounced during every event or every solute. Looking at the distribution of the values in the boxplots (figures 4.9, 4.12, 4.15, 4.18, and 4.21), there are solutes and events where less change in concentrations are found.  $\Delta^{18}\text{O}$  only showed little variation in E4 and E5, DOC concentrations barely changed during the intermediate events E2, E3, and E4, all anions show a tendency to being less strongly variable during E4 and E5, chloride and nitrate concentrations also showed little variation during E2, and potassium concentrations, too, show a decline in variation range during the last two events (E4 and E5). All in all, there seems to be a general tendency to experiencing a less pronounced change in chemistry during the later event(s), which is in line with the assumed re-connection of groundwater that acts as a stabilizer on stream chemistry. Overall, these findings of streamwater chemistry change upon rainfall are in accord with what is found in current literature; for example, Bernal et al. (2019), Fovet et al. (2018), or Moatar et al. (2017), all found that streamwater chemistry in headwater streams usually changes over the course of a rain event, be it increasing or decreasing solute concentrations.

### 5.2 CHEMISTRY CHANGE AS A FIRST FLUSH, THE EXTENT OF WHICH IS DEPENDENT ON THE DURATION OF THE EVENT-PRECEDING DRY PERIOD

The change in streamwater chemistry mentioned above was hypothesized to happen in the form of a first flush, i.e. that solute concentrations would increase drastically in the beginning of the event upon onset of flow, to then decrease more slowly over the rest of the event and ultimately return to baseflow values. Butturini et al. (2008), for example, found that storm events cause solute flushing in streams on a short timescale, which would be in accord with my hypothesis. When looking at the timeseries (figures 4.7, 4.10, 4.13, 4.16, and 4.19), however, this type of behavior is rarely seen. E1, which was the event where the biggest flush was expected due to the accumulation of salts and organic material over the course of the dry period (Romani et al., 2006; Skoulikidis & Amaxidis, 2009) did not show a first flush behavior, but rather a seemingly random wash-out of solutes. The

concentrations measured in this event were not necessarily the highest out of all five, though the range (save possible outliers in later events) was in fact the highest for many solutes (DOC, nitrate, sulfate, potassium calcium) (figures 4.9, 4.12, 4.15, 4.18, and 4.21; table 2 solute range). This implies that there is a type of flush going on during this event, just not the one that was expected. In my opinion, finding this pattern in this headwater catchment also makes sense when considering the inputs and processes involved. The stream network had been lying dry for a long period of time, accumulating all sorts of materials, which were then beginning to be washed out during E1. Flow first had to be re-established around the sampling locations, giving new pulses of little flushes and dilution periods throughout the event, leading to strong fluctuations over a wide range.

The concentrations of DOC were expected to increase during the rain events, as has been a widely reported response from multiple climate systems (Vaququez et al., 2014). They found that DOC maxima occurred during the rewetting period as the rainfall triggered the flushing of DOC. Bernal et al. (2005), Romání et al. (2006), and Harjung et al. (2018) all found a massive increase in DOC concentrations in the streamwater due to rainfall. Compared to the concentrations they found (max. of 18 mg/l), the values for DOC concentrations found in the Diebis were much higher (39.1 mg/l on average over all measurement locations during E1). What was not found, however, was this increase in DOC upon rewetting, or a general first flush pattern. DOC concentrations measured during baseflow prior to E1 were also much higher than what was found during E1 (60.8 vs. 39.1 mg/l), thus contradicting the current literature. This may be explained by a very small rain event shortly before E1, which had already flushed out some of the DOC accumulated in the streambed, or due to continuous leaching and other terrestrial input in stagnated pools that were measured prior to E1. As previously stated above, while a traditional first flush cannot be detected in E1, the concentrations and their range are much higher than what was found in the succeeding three events, thus still behaving in a flushing behavior.

Now looking at the streamwater chemistry change a little more closely, with EC as a good indicator of the amount of ions dissolved in the streamwater, as it increases the more salts are brought into solution. As such, EC was expected to be highest in E1, and suddenly increase in the beginning of every event to correlate with the hypothesized first flush behaviour. Salts accumulate during the dry period, and thus increase EC during this time (Skoulikidis et al., 2017; Kiweiet et al., 2019). This, and that the EC values measured during the first baseflow measurements done prior to E1 were really high, further raised the value of EC expected to be seen during E1. Looking at the EC values, however, they do not concur with these hypotheses. EC was not higher in E1, in fact, when taking the average of the three locations, E1 exhibited the lowest EC values of all five events, and E5 the highest of the whole sampling season (average of all EC measurement per event: E1 = 488  $\mu\text{S}/\text{cm}$ , E2 = 503, E3 = 500, E4 = 525, E5 = 556  $\mu\text{S}/\text{cm}$ ). EC in E1 was also lower than what was found during the first baseflow measurements. This implies that more ions were dissolved in the streamwater prior to, and in all events after E1, which is actually the exact pattern seen in chloride, sulfate and calcium, and, except for the higher concentrations prior to E1, also in nitrate and potassium ions. Chloride and sulfate both had their highest ion concentrations during E5, while nitrate-, potassium-, and calcium- ion concentrations were highest during one of the intermediate events (table 2 solute range). What was also supposed to be observable was a first flush during all events, which would come with an increase in EC in the beginning of the events. However, this was not found either. E2 and E3 showed a decrease in EC over the course of the event, while E1, E4 and E5 showed an increase, if anything. The decrease of EC can be explained by discharge dilution watering down the ion concentration, which would be in line with the high event-water fractions found in these two events (table 1 event characteristics), and also with what Skoulikidis et al (2017) found while doing their experiments. The increase in EC, however, would rather point to a belated flushing of certain ions.



When comparing the ions to EC per event, the concentrations of the anions are highly erratic during E1, which coincides with the EC. The cation concentrations, too, were fluctuating strongly throughout the event, which, again, is in line with what was found in EC. What may be an explanation for this behavior is that, as more parts of the stream network began to flow, salts were washed out throughout the event all over the catchment, resulting in what appears to be a random behavior. When looking at what values can be found in the literature, one finds that sulfate and chloride usually increase during the dry period, while nitrate concentrations would decrease over the same time span (Vazquez et al., 2007; Skoulikidis et al., 2017). While sulfate and chloride concentrations were actually higher during baseflow conditions prior to E1, the difference was marginal, as was the difference of nitrate concentrations before and during E1. Nitrate is usually found to spike drastically after the summer drought (Bernal et al., 2005, Skoulikidis et al., 2017), and to have a positive relationship to discharge, with nitrate concentrations peaking a little after the hydrograph (Bernal et al., 2005; Rusjan et al., 2008). In my case, nitrate concentrations were highest much later in the sampling season, e.g. during E5. This could be explained by what Welsch et al. (2001) found, who said that nitrate-rich groundwater is flushed into streams, thus viewing groundwater input as a controlling factor on nitrate concentrations which only came into effect well into the sampling season. The concentrations I found for nitrate were relatively high when compared e.g. to Bernal et al., 2019, who found 0.2 to 0.3 mg/l, while I found concentrations up to over 5 mg/l (table 2 solute range).

Coming back to the first original hypothesis, no traditional first flush behavior was seen in any of the events or solutes, except for a potentially diluted one in sulfate and potassium ion concentrations during E2 and E3. The solute concentrations either increased and decreased more or less erratically over the course of the event (e.g. all solute concentrations during E1,  $\text{SO}_4^{2-}$  concentrations during E3, or  $\text{Ca}^{2+}$  concentrations during E4), or behaved in a more constant fashion (e.g. DOC concentrations during E2, E3, and E4,  $\text{Cl}^-$  concentrations during E2 and E4, or  $\text{NO}_3^-$  concentrations during E5). What was found more often was a dilution effect during the intermediate events, whereby the solute concentrations would decrease due to a dilution by the high event-water fractions.

Overall, of all solutes, the generally largest range in solute concentrations were found during E1, while the smallest were found during E5, which correlates well with the assumption of a larger flush during the first rainfall after a period of drought, the accumulation of organic matter expected in the streambed, and the change from a more rain-fed (intermittent) to groundwater-fed (perennial) stream system. However, there are also many solute concentrations during later events that were equally high or higher, contradicting the statement that the biggest flush happened during E1.

### 5.3 EXTENT OF FLUSH CORRELATES WITH RAIN INTENSITY

The extent of the flush, i.e. the change in concentration and their range on per event and location was expected to be smaller during low-intensity rainfalls and higher during high-intensity rainfalls. However, the differences in fluctuation behavior and range between E1 and E5 do not coincide with differing precipitation intensities, as these two events actually had a similarly low average rain intensity (table 1 event characteristics). There, the decisive factor must not have been intensity, but rather groundwater connectivity. The event with the highest average precipitation intensity, as well as the highest total precipitation, was E3, which, when compared to E2 and E4, does seem a little more erratic (figures 4.7, 4.10, 4.13, 4.16, and 4.19). According to the hypothesis, the solute concentrations found in this event should be higher and show a pronounced first flush behavior. As it is, the concentrations of most solutes are not particularly high, and appear to show more of a dilution effect rather than a first flush ( $\text{EC}$ , sulfate-, potassium-, and calcium ions), or are generally quite stable (DOC, chloride- and nitrate ions). The dilution effect is something also seen in other literature, where solute concentrations are inversely correlated with rainfall intensities and duration (Tiefenthaler & Schiff, 2001), which they explain as

more rain dilutes the concentration maxima of the original first flush. The stable and very low DOC concentrations are opposing to Delpla et al.'s (2011) findings, which found what was hypothesized, that the export of DOC during high intensity events is higher than during lower intensity rainfalls. Especially sulfate and potassium concentrations do show a bit of a peak in the first half of the event, though, which is still reconcilable with the above-made statement when considering that the increasing discharge prevailed over the flushing (Skoulikidis et al., 2017).

All things considered, there might be a small correlation between the extent of a flush and rain intensity if there were no other influencing catchment parameters such as groundwater connectivity, as may be assumed from the findings in E3. However, comparing the three intermediate events, and taking event duration into account, one is even less prone to see a correlation between concentrations and precipitation intensity, as during E2, which was considerably less long than E3 and E4, and a lower maximum hourly precipitation intensity, solute concentrations that were similar in to what was seen during the other two events were found. This implies that during these events, too, a different process is involved in determining the extent of the flush.

#### 5.4 SPATIAL VARIATION WITHIN THE CATCHMENT

##### 5.4.1 SPATIAL VARIATION BETWEEN SSS DURING E2

$\Delta^{18}\text{O}$  showed a tendency to increase, i.e. become less negative, when moving downstream, which reflects the increasing portion of rainwater accumulating in the surface runoff while moving through the catchment. EC showed an increase further downstream when multiple reaches come together, which makes sense when considering the longer stream network that can pick up and wash out solutes into one reach. Higher values were found in the more eastern part of the catchment (the reach going through location C), which coincides with reaches running through forested parts of the catchment, which is likely why the EC is higher there. DOC concentrations follows a similar pattern in the SSS in the lower part of the catchment, but the opposite on most of the other measuring locations. The samples taken in the SSS showed much higher DOC values than the Isco streamwater samples, which can be explained by the fact that the streams going through the SSS locations weren't completely washed out during E1, meaning that they might still have been flushing out organic carbon collected during the summer drought. Also, Bernal et al. (2019) suggested that DOC concentration/discharge responses show high variability in intermittent streams due to low hydrological connectivity which lead to pockets of DOC accumulation. The patterns found in the three anions (chloride, nitrate, and sulfate) were expected to align with the pattern found for EC, which is the case in about half the samples taken with SSS. The sample taken at the very top of the catchment was much higher in chloride and nitrate than the EC would lead one to believe, however, the concentrations found in sulfate coincides with the measurements done for EC. As the concentrations of sulfate were much higher than the concentrations of chloride and nitrate, this pattern indicates that sulfate was the dominant ion when determining EC. Nitrate and sulfate concentrations had a very similar pattern, which differed from what was found for chloride. Chloride had higher concentrations further up in the catchment, while nitrate and sulfate concentrations increased further downstream (except for the SSS in the middle of the catchment located in coniferous forest, which had the highest concentrations of nitrate and sulfate), indicating a spatially varied input of these cations. McGuire et al. (2012) said they found a very fine scale spatial dependence of nitrate ion concentrations, suggesting in-stream uptake happening over very short flow-connected distances, which is in line with the here findings, especially in the lower half of the catchment.

##### 5.4.2 SPATIAL VARIATION BETWEEN LOCATIONS A, B, AND C

The spatial variation between the three locations can be best assessed when looking at the boxplots of each solute or solute group (figures 4.9  $\delta^{18}\text{O}$ , 4.12 EC, 4.15 DOC, 4.18 anions, 4.21 cations). There are two recurring patterns that are found when inspecting these boxplots more closely. One is that location B reacts differently from the other two locations, most of the time the concentrations on this location are much lower than on the

other two. Location B exhibits lower values for  $\delta^{18}\text{O}$  during E1, E4, and E5, for EC during all events, for nitrate E3 and E4, for sulfate during all events, and for calcium during all events except for E1. Higher values on location B could also be found, but only for potassium (E2, E3, E4, and E5).

The second pattern that can be observed is that higher concentrations were found on location C. This pattern could be observed in the two anions chloride and nitrate during E2, E3, E5, and just E3, respectively. This coincides with the pattern found when looking at the hysteresis classes, where solutes on location C often showed an initial decrease from the baseflow values, while locations A and B exhibited an increase from the same, also indicating at least some spatial variation. Location A was both influenced by location B and C, the hydrochemical parameters measured there usually resembled one of the two other sampling sites. This was unexpected, as location A was thought to become more different from the other locations as the stream there started to become more perennial-like. However, locations B and C had also started to have constant flow at around the same time as location A, so no real comparison between still-intermittent and already-perennial can be made. Five events are not enough to really be able to tell something about the goings-on in spatial variabilities, but at the moment it looks as though no event showed more pronounced spatial variation, indicating no change in pattern in relation to the stream network becoming more permanently connected.

Overall it can be said that there appears to be at least some spatial variability in this catchment, which one can assume from both the results gotten using the single stage samplers, as well as from the comparison of just the three Isco sampling locations. The extent and certainty of this spatial variation depends on the solute that is being studied, as for example DOC barely varies between the three Isco locations during an event, while it does show quite a range in concentrations when looking at the measurements gotten with the SSS during E2 (ranging from roughly 4 to 70 mg/l), which were collected farther across the catchment. These findings support the findings of Hale & Godsey (2019) which also stated that high spatial variation, especially in DOC, can be expected from a headwater catchment, with variation decreasing with downstream flow distance (McGuire et al., 2012).

### 5.5 STREAMWATER-C CHANGES FROM ORGANIC TO INORGANIC OVER TIME

As the highest concentrations in DOC were expected in E1, the  $\delta^{13}\text{C}$  ratios were also expected to be closest to the ratio of organic matter. OM found in the streamwater mostly originates from litterfall (Palmer et al., 2001), especially so during the first rainfall after a long litter-accumulation period during drought. The values would be expected to be ranging from -29.5 to -26 ‰, as that is the value most common for C3 plants (Balesdent et al., 1993; Palmer et al., 2001). However, ratios this low weren't found, rather, they were mostly much less depleted. This can be explained by two possible reasons. For one, a good part of the catchment consists of meadow covered in plants of the family of the Poaceae, which have high  $\delta^{13}\text{C}$  values ranging from -19 to -6 ‰ (Smith & Epstein, 1971), which is much closer to the values found in the streamwater samples. It is thus possible that the DOC source is not only leaf litter, but also finds input from grasses. The second explanation needs inorganic carbon. As the bedrock of the catchment mostly consists of limestone, a lot of carbonate minerals are dissolved during rainfall and transported off, thus influencing the carbon isotopic composition of the streamwater. Other studies have found  $\delta^{13}\text{C}$  values of streamwater inorganic carbon from anywhere between -21.5 and 0 ‰, which is more in line with my findings, however, many of these studies were conducted on river systems much larger than the Diebis bach, meaning that the  $\text{CO}_2$  production right in the water column would likely be significant (Palmer et al., 2001, referring to Atekwana & Krishnamurthy 1998; Pawellek & Veizer 1994; Yang et al. 1996). Still, dissolved inorganic carbon exhibits much lower values than dissolved organic carbon, so these values can be used as a comparison supporting the low  $\delta^{13}\text{C}$  values found in my stream samples. Therefore, the more the isotopic composition of the water samples resembled that of the rock sample, i.e. the less depleted in  $\delta^{13}\text{C}$  the water was, the more IC was dissolved in the water as compared to OC. If the  $\delta^{13}\text{C}$  ratio was close to the ratio

found in the rock, but the DOC concentrations measured were also high, both DIC and DOC were abundantly dissolved in the water, and it indicates that they might be following the same pathways. This pattern was seen in E5, during which very high concentrations of DOC were found, along with  $\delta^{13}\text{C}$  ratios very close to the rock's values (figure 4.22  $\delta^{13}\text{C}$  -DOC). E3 exhibited more negative  $\delta^{13}\text{C}$  ratios, coupled with very low DOC concentrations, as did E2 and E4. This again hints at similar pathways of DOC and DIC, as the ratio of the two does not appear to change much between the events. E1 lay in between E3 and E5 both in terms of DOC concentrations and  $\delta^{13}\text{C}$  ratios, meaning that the DOC/DIC ratios again stayed similar, supporting again the claim of similar pathways that DOC and DIC follow in this catchment. Over a short-term temporal scale, the behavior of  $\delta^{13}\text{C}$  was not always the same on every location. During E1, the streamwater became less depleted over the course of the event, which indicates a decrease in DOC as the DOC/DIC ratio shifts towards DIC (figure 4.23). As no first flush behavior could be observed during this event which would explain the decrease of DOC in the streamwater, an increase in DIC is assumed, which could be caused by rainwater input. DIC in precipitation has been found to be between -22.2 and +0.2 ‰ (Górka et al., 2011), and since the rise to less negative values was found towards the end in the last third of the event when also most rain water fell (figure 4.1), it is possible that the rain fall had low DIC values. During E3, the ratio of DOC to DIC remained more or less constant over the course of the event, as neither  $\delta^{13}\text{C}$  ratios, nor DOC concentrations changed a lot with rainfall. E5 was the event where the three locations differed the most in their reaction of  $\delta^{13}\text{C}$  over the course of the event. The water of location A became less depleted in  $\delta^{13}\text{C}$  over the course of the event, which again implies a shift in the DOC/DIC ratio towards DIC. Here, this could be due to the connection of the groundwater to the stream network, as groundwater has been found to contain more DIC than riverwater (Meredith et al., 2016). The opposite of this is shown on location B, however, where the streamwater had  $\delta^{13}\text{C}$  values very close to the rock's ratios, to then drop and become more depleted in  $\delta^{13}\text{C}$  towards the end of the event (figure 4.23). This drop correlates with an increase in DOC concentrations found on this location, which shifts the DOC/DIC ratio towards DOC for once, lowering the  $\delta^{13}\text{C}$  values. Location C looked very similar to E3 in terms of  $\delta^{13}\text{C}$  ratios, but with much higher, though also quite stable, DOC concentrations. As the  $\delta^{13}\text{C}$  values found on location C during all events was always at least a little lower than what was found for the other two locations (figure 4.22), thus making this a recurring result, it can be assumed that this indicates a high DOC input that overpowers the fraction of IC also dissolved in the streamwater, or that only little DIC is available on this location.

To address the last hypothesis constructed in the beginning of this thesis in short, the ratio of DOC/DIC of the dissolved carbon in the streamwater is more stable than assumed over the course of the whole sampling season, however, short-term temporal variability is possible over the course of an event, whereby most of the time the portion of DIC does in fact increase. This is likely to be due to rain and groundwater inputs, not because all DOC is suddenly being flushed out.

## 6 CONCLUSION

In the course of this thesis it was to be elaborated how stream chemistry in an intermittent stream changed in response to five rainfall events, differing in length and intensity, in late 2018. Intermittent streams are characterized by a repeated cessation and onset of flow, a cycle which influences both their ecology and their hydrochemistry. They represent more than half of the global stream network, and are expected to further increase in abundance due to climate change and human water stress. Up until recently only very little interest has been paid to them, and little is known about their biogeochemical reactions, and their share in the global water and nutrient cycles keeps being underestimated. To help shed some light on the reactions of stream chemistry to rain fall, a study was conducted in a small temperate headwater catchment close to Zurich. It was hypothesized that stream chemistry would change as solutes were beginning to be flushed out by the rainwater input (small-scale temporal variability), that this change would depend on the sampling site (spatial variation)

and that this change would differ depending on antecedent soil moisture conditions and duration of dry period (larger-scale temporal variability). For this, streamwater samples were taken on three locations distributed over the field site over the course of five rain event, making sure to catch the onset of flow. In addition to these samples, 29 smaller samplers that would fill up upon onset of flow were also installed to take samples during rainfall. These streamwater samples were analyzed on several hydrochemical parameters:  $\delta^{18}\text{O}$ , EC, and DOC,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  concentrations. Some samples were also tested on their  $\delta^{13}\text{C}$  ratio to determine the streamwater carbon's origin.

It was found that streamwater chemistry did change over a rainfall event, with the tendency to a decreasing extent of said change over the sampling season i.e. wider hydrological connectivity and a higher groundwater input that has a stabilizing effect on solute concentrations, thus lessening the effect of a higher solute input due to rainfall.

Concerning the question of a first flush behavior it was seen that there were only few solutes during few events that might have behaved in a diluted version of the traditional first flush ( $\text{SO}_4^{2-}$  and  $\text{K}^+$  during E2 and E3), thus disproving the hypothesis of a first flush behavior in all solutes during every event. What was seen was erratic behavior of the solute concentrations over time, which decreased over the course of the sampling season due to the washing out of the stream bed, the increasing hydrologic connectivity of the stream network, and the re-connection of the groundwater with the stream. For some events and solutes, a dilution by the high event-water fractions was observed.

E1 was hypothesized to have the biggest flush of solutes of all events, which on the one hand was concurred with the overall largest range in solute concentrations found during this event, and on the other hand rebutted as, depending on the solute, similar or even higher concentrations were found during later events.

Furthermore, the extent of the flush did not show a visible correlation with precipitation intensity, but more likely with hydrologic connectivity and groundwater input. More precipitation actually leads to dilution rather than a more pronounced flush, while less precipitation still leads to concentrations that are similar to what is found in events with higher rain intensities.

Moreover, spatial variation was found both between the samples taken by the single stage samplers during E2, as well as between the samples taken by the Iscos during all five events. The extent of this variation depended on the solute and the event during which it was measured. Variation was either found between samples taken in a more forested part versus samples taken from locations that are more strongly influenced by a meadow, or between samples taken more upstream versus samples taken more downstream in the catchment. Spatial variation between the SSS during E2 was biggest for DOC, which may be due to pockets of DOC accumulation caused by low hydrological connectivity (Bernal et al., 2019). Spatial variation between the three Isco locations during all other events was characterized by either location B having much lower values than A and C, or that location C showed much higher concentrations than locations A and B. The concentrations found on location A usually resembled either the values found on location B or on location C, which was surprising as it was hypothesized that there would be more variation between what was thought to be a more perennial-like location such as location A, and the more intermittent parts like locations B and C. However, all these three locations started to flow more permanently at about the same time, which made this comparison impossible. Spatial variability was found during all five events, indicating no change in pattern in relation to an increase in hydrological connectivity of the stream network.

Lastly, contrary to the original hypothesis that the ratio of DOC/DIC would change over the course of the sampling season due to a flushing out of DOC in the beginning of the season, the DOC/DIC turned out to be quite stable in longer-term temporal variation, while the DIC fraction sometimes showed an increase in small-scale temporal variability, probably due to outside water inputs (i.e. groundwater higher in DIC) increasing the DIC concentration in relation to a stable amount of organic carbon.

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## PERSONAL DECLARATION

Personal declaration: I hereby declare that the submitted thesis is the result of my own, independent work.  
All external sources are explicitly acknowledged in the thesis.

Zurich, 30. September 2019.

A handwritten signature in blue ink is written above a horizontal dotted line. The signature is stylized and appears to be 'M. J.' followed by a long, sweeping horizontal stroke.