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Spatial and temporal variability in streamflow chemistry in two small pre-alpine catchments

GEO 511 Master's Thesis

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Picture cover page: view from upper catchment in the study area in the Alptal towards the great and the small Mythen 31 October 2016

Abstract

Few studies have documented changes in stream flow and chemistry along headwater streams because of the difficult accessibility and because it is assumed that the spatial variability along these small streams is small. However, headwater streams are of great importance because they account for 70-80% of the total flow channel length of the river networks, contribute significantly to runoff and influence stream- and river sections downstream. In order to gain more knowledge about the spatial and temporal variability in streamwater chemistry and isotopic composition and to determine groundwater source areas contributing to baseflow, four snapshot sampling campaigns were conducted in two subcatchments of the Studibach catchment in the Alptal valley (SZ) in Switzerland during the summer of 2016. Two continuous salt tracer experiments were done to quantify and verify the groundwater contributions inferred from the sampling campaigns. There was a large spatial variability in stream chemistry (EC, Ca^{2+}, Na^{+}, Mg^{2+}, Cl^{-}, SO_4^{2-} and δ^2H) along the different stream branches in the two investigated catchments. Areas and sections, where groundwater contributes to the streamflow were identified by the snapshot sampling campaigns, as well as by the continuous salt tracer experiments and suggest inflow of shallow and deep groundwater at specific sites. Groundwater contributions to the stream were related to changes in topography, but there was no correlation between land use and the spatial variability of streamwater chemistry. The results from this study show not only that stream water chemistry can vary over very short distances but also that snapshot sampling is a very good method to detect spatial and temporal variability in streamflow and groundwater contributions to the stream. Continuous salt tracer measurements allow detection and quantification of the groundwater contribution to the streamflow. As both methods are relatively easy, further measurements on headwaters and small streams are desirable and needed to gain more knowledge about these important streams.

Key words: streamflow generation, snapshot sampling, continuous salt tracer experiment, groundwater source areas, temporal and spatial variability in hydrochemistry

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Nadja Grunder, June 2017

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Abbreviations

API	Antecedent Precipitation Index
C	Catchment (C21 = catchment 21, C32 = catchment 32)
Ca^{2+}	Calcium (mg/l)
Cl^-	Chloride (mg/l)
cm	Centimeter
DEM	Digital Elevation Model
δ^2H	Deuterium (‰)
EC	Electric conductivity (µS/cm)
ha	Hectares
m	Meter
m a.s.l.	Meters above sea level
Mg^{2+}	Magnesium (mg/l)
min	Minute
Na^+	Sodium (mg/l)
SC	Sampling Campaign (SC2 = 19.07.16, SC3 = 31.08.16, SC4 = 05.10.16, SC5 = 31.10.16)
SD	Standard Deviation
SO_4^{2-}	Sulfate (mg/l)
TWI	Topographic Wetness Index

Introduction

High flows in rivers and creeks, floods and extreme rainfall events; these are some hydrological topics that regularly reach the media, that appear on television and that are therefore seen by the general public. Floods frequently damage human infrastructures and natural habitats. Large rivers as the Amazon, the Nil or the Colorado river are known for their massive amounts of water, their extreme force and their extensive spatial expansion. But aren't all the well-known rivers fed by a network of smaller streams in the upper zone of their catchment? And what about the wetness stage between high flows and dry periods?

Rivers and streams cover about 0.3-0.6 % of the lands surface on earth (Downing et al., 2012). Small streams at the origin of river systems are often called headwaters and account for about 70-80% of the total flow channel length of the river networks (Wohl, 2017) and contribute significantly to runoff in general and to baseflow in particular (Tetzlaf and Soulsby, 2008). Furthermore, Wohl (2017) indicates the importance of the influence of these headwaters on the stream network further downstream. Sediments and nutrients that are transported to downstream areas affect streamflow chemistry and thereby plant and animal habitats. Because people are less likely to see the importance of headwaters compared to other stream- or river sections (Wohl, 2017), an issue that might be because the headwaters do not affect them directly, and because hydrochemical measurements and observations are more difficult in mountainous areas (Fischer et al. 2015), headwaters are still largely unmeasured (Bishop et al. 2008). Furthermore, headwaters in mountainous catchments are often characterized by a very heterogenous landscape, steep slopes, high amounts of precipitation and shallow soils (Fischer et al. 2015). In order to close research gaps, Wohl (2017) suggests to especially focus on further research on the mapping, hydraulics and sediment regime, and the connectivity of the headwater stream channels.

Groundwater is a significant component of streamflow in general (e.g. Soulsby et al., 1998; Tezlaff and Soulsby, 2008; Müller et al., 2010) and while baseflow conditions, groundwater is the main source for streamflow (e.g. Mulholland, 1993; Burns et al. 1998; Welch and Allen, 2012; Hölting, Coldewey, 2013). After intensive rainstorms, the runoff of the stream increases significantly. On the one hand due to the contribution of precipitation and fast runoff processes, on the other hand, due to increasing baseflow contributions (Maident, 1992 (Fig. 1); Hewlett, 1974). Groundwater normally has higher solute concentrations due to the mineral weathering (Egusa et al., 2016) and (except in winter) lower temperatures than stream water. Because of the contributions from groundwater to streamflow, the hydrochemistry (Anderson et al., 1997; Asano et al., 2003; Uchida et al., 2003; Soulsby et al., 2007) and the temperature (Sear et al., 1999), and thereby stream ecology is influenced.

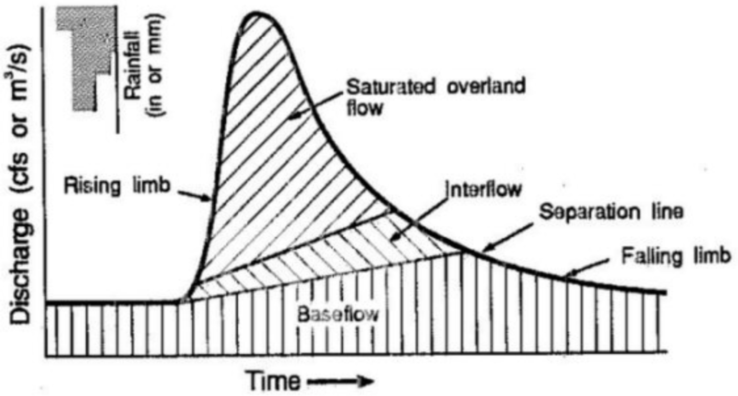


Figure 1: components of a river hydrograph from Handbook of Hydrology, Maidment (1992)

The chemical composition of groundwater depends on multiple different temporal and spatial factors: for instance geology, soil, land use and time since infiltration (e.g. Hölting and Coldewey, 2013; 113f). The extent of influence on groundwater chemistry depends largely on flow path ways and thereby transit time of the water.

Groundwater reappears at the surface (e.g. as a spring) at specific sites, mostly at decreases or sudden changes in slope where the space for groundwater flow is minimized be the bedrock and surface getting closer together or by at disruption zones in the bedrock, where groundwater from deeper layers with high groundwater flow resurface (Hölting and Coldewey, 2013; 57f).

In order to identify groundwater source areas to the stream and investigate their flow paths, tracer methods are widely used (e.g. Rodgers et al. 2004; Barthold et al., 2010; Hrachowitz et al., 2011; Inamdar et al., 2013; Lu, 2014; Mallard et al., 2014; Orlowski et al., 2014; Penna et al., 2014; Singh et al., 2016). Salt is often used as a tracer because it is accessible and affordable.

Researchers often choose to focus on spatially distributed sampling (e.g. Fischer et al., 2015; Müller et al., 2010) in order to gain process understanding (Fischer et al., 2015). Few studies are sampling along the streams on a high spatial resolution (e.g. Likens and Buso, 2006; Zimmer et al., 2013; Egusa et al., 2016; Singh et al., 2016). Likens and Buso (2006) measured at a 100 m interval while Egusa et al. (2016) and Zimmer et al. (2013)

measured along a stream in a ± 50 m interval. Egusa et al. (2016) did not continue the measurements up to the spring zone. Instead, the outlet of these headwater areas was measured. Singh et al. (2016) measured frequently along the stream branches (± 20-30 m interval) of two headwater streams.

Benjamin Fischer et al. (2015) reported the findings of three snapshot campaigns using the temporal and spatial variability to distinguish contributing sources to baseflow. No significant inter- or intra catchment variability in hydrochemical- or isotopic composition was observed. Shallow groundwater samples were significantly different from streamwater samples. No or only very little interaction between wetlands and streamflow was measured. Slight hydrochemical and isotopic changes were observed from the sub-catchments spring zones to the outlets.

Likens and Buso (2006) and Zimmer et al. (2013) focused on fine scale spatial and temporal variations in stream water chemistry. Linkens and Buso (2006) mapped small temporal changes between the two seasons (May-July and October-December) but found large changes in stream chemistry throughout the whole catchment. The changes in stream water chemistry were related to changing vegetation, geologic substrates and wetland areas.

Zimmer et al. (2013) observed spatial as well as temporal variability in all sampled water types (stream- and groundwater). Upstream sources were found to be more variable than the measured downstream sources. This dilution from upstream to downstream was correlating with the increasing upslope accumulating area.

Egusa et al. (2016) measured stream discharge at 113 points and baseflow water chemistry at 159 points and used end-member mixing analysis to seperate the stream water into subsurface water and groundwater. Large variability in both, groundwater and subsurface water contribution was observed in catchments with an area < 1km^2. With increasing catchment area, the contribution from subsurface water decreased and the contribution from groundwater increased. Detailed chemical analysis for spatiotemporal variability was not performed.

Singh et al. (2016) sampled groundwater, baseflow (each 25 m along the streams) and precipitation each month from June 2011 until June 2013 and analysed them for stable isotopes (^{18}O and ^{2}H). Temporal as well as spatial variability of δ^{18}O along the streams was observed. Stream water became enriched in ^{18}O from the heads of the catchments to the outlets. Spatiotemporal variability in baseflow δ^{18}O correlated positively with the arrangement of the hillslopes in the catchments.

This master thesis is follows up on the research of Fischer et al. (2015). Focus lies on the spatial and temporal variability in two small sub-catchments of the Studibach catchment, which was one of the sub-catchments of Fischer et al.'s study area, and is a sub-catchment of the Zwäckentobel area in the Alptal. High spatial resolution snapshot sampling campaigns were conducted in the summer of 2016.

Research Questions

The goal of this master thesis is to provide more knowledge about spatial and temporal variability in streamwater chemistry and groundwater source areas contributing to baseflow in temperate, humid, pre alpine catchments. The following research questions are adressed:

1. *What is the spatial and temporal variability in the chemical and isotopic composition of groundwater and streamwater during baseflow conditions?*
2. *What are the groundwater source areas that contribute to baseflow? Where does groundwater flow into the stream?*
3. *Is the variability in the isotopic and chemical composition of streamflow related to topography or land-use?*
4. *Are measurements at the outlet of a catchment representative of the entire catchment?*

The first research question demands a general overview on groundwater and streamwater chemistry, chemical patterns and changes over the season in the selected catchments. The second question aims to provide answers to where groundwater flows into the stream and where this groundwater originates from. Does the groundwater flowing into the stream, come from one groundwater source area or is it a mixture of different groundwater source areas? Furthermore, we want to assess if snapshot sampling is an appropriate method to observe groundwater inflows into the stream. In addition to the hydrochemical analyse, salt tracer experiments were used to help understand the complex interactions between groundwater and streamflow. The third research question aims to find a reason for the observed variability or a way to predict this variability. I.e. can we find groundwater inflows to the stream at topographically similar areas? The fourth research question deals with the representativeness of measurements at the catchment outlet. In most catchment hydrological studies samples are only taken at the stream outlet. This thesis comments on whether these outlet measurements represent the hydrological processes in the catchment.

Context of this thesis within ongoing research in the Alptal

Ongoing projects in the same research catchment started in spring/summer 2016 and focus on the variability in shallow groundwater chemistry and runoff generation processes (PhD project Leonie Kiewiet), stream network expansion and contraction (PhD project Rick Assendelft) and the occurrence and chemical composition of overland flow (Msc Thesis Tobias Sauter). Research in a neighbouring catchment focuses on high temporal resolution monitoring of stream chemistry (Dr. Jana von Freyberg, ETH) and the importance of snow on lowflows (PhD project Andrea Rücker, ETH/WSL). The fact that these projects are conducted in the same or in similar catchments at the same time, provides possibilities for intercomparison of the data and results.

Previous studies in the Alptal area

Feyen et al. (1996) performed a study on runoff processes in catchments with small scale topography and showed that surface and subsurface runoff responded quickly to rainfall inputs in the catchments and in the soil plots. This indicated the dominance of fast-flow paths, such as cracks and fissures. Feyen et al. (1999) studied flow paths of water in a forest soil, in the alptal area with a tracer experiment. While the reaction was extremely fast, when the tracer was injected directly into the gleyic sub-soil, much slower breakthrough times were measured when tracers were applied onto the soil surface.

Zehnder (2013) measured the hydraulic conductivity using slug tests and compared her results to site characteristics such as topography and vegetation but found no significant correlation between the hydraulic conductivity and the tested topography factors (plan curvature and slope). K_{sat} values tended to decrease with decreasing soil horizon depth.

Herrmann (2014) wrote his master thesis about the dynamics and processes of runoff generation in the Studibach catchment in the Alptal. His results showed that the catchment area and the topographic wetness index (TWI) are good predictors for the median runoff as well as for the reaction time of the electrical conductivity (EC).

Rinderer et al. (2016) monitored groundwater continuously at 51 groundwater sites in the pre-alpine Studibach catchment from September 2010 to November 2012. The sites were distributed in different topographic positions, land use zones and soil types. Their results showed a correlation between groundwater response timing and topographic characteristics and contributing upslope area. Comparing their results to previous studies, they suggest that in catchments with less permeable soils, groundwater response timing is more affected by surface topography than by the rainfall characteristics and antecedent soil moisture conditions.

Rinderer et al. (2014) studied the topographic controls on shallow groundwater levels and when TWI assumptions are valid in the Studibach catchment. They found that median groundwater levels were correlated to topographic characteristics like slope, curvature and TWI but this correlation depended on whether the local topography or the topography of the upslope contributing area was used. While comparison of the mean groundwater level with the local slope (%) resulted in a stronger correlation than comparison with the mean slope of the upslope contributing area, the comparison of the local curvature with the mean groundwater level resulted in a weaker correlation than the the comparison of the mean curvature of the upslope contributing area.

The study of Fischer et al. (2015) about the contributing sources to baseflow, mentioned earlier in this chapter and the research on pre-event water contributions to runoff events by Fischer et al. (2016) are two more important studies conducted in the Alptal area. Fischer et al. (2016) investigated how precipitation and catchment characteristics such as land use, slope and geology determine the contribution of event- and pre-event water to stormflows by sampling streamwater and runoff of 13 different rainstorms. The pre-event water contribution of the headwaters varied more between the different events and not so much between the different catchments, although the land cover varied clearly between the catchments. Increasing rainfall amounts resulted in proportionally more rainfall in run-off.

Study Site Description

The Alptal valley is located in the central Swiss Prealps in the canton of Schwyz (Fig. 2). The valley stretches from Einsiedeln (882 m a.s.l.) in the north towards the two Mythen Mountains (1’438 m a.s.l. and 1’898 m a.s.l.) in the south. The annual precipitation is 2300 mm y^{-1}, 30% falls as snow between December and May (Feyen et al. 1999). Groundwater tables (Rinderer et al., 2015) as well as streamflow (Fischer et al., 2016) react quickly to precipitation.

Figure 2: Location of Alptal (SZ) in Switzerland

The Studibach catchment is located at 697’911/210’585 (Swiss coordinate system). The catchment size is about 20 ha and ranges in altitude from 1’270 m a.s.l. in the west up to 1’650 m a.s.l in the east. The catchment has a west to south-west aspect; the average slope is ~ 21° (Fig. 3a). The Studibach catchment can be divided into seven nested sub-catchments (see Fig. 3 and Table 1). Their size varies from ~ 0.2 ha to ~ 20 ha and their mean slope angle ranges from 19° to 25°. In the upper parts of the catchment, variation in slope steepness is significant and can be a reason for the many stream heads in this area. In the steepest sub-catchments (C11, C21, C12), there are many small landslides.

The geologic formation is flysch, consisting of alternating calcareous sandstones with argillite and bentonite schists (Schleppi et al., 1998). Three different types of flysch outcrop in the catchment: Schlieren Flysch in the upper spring zone, Wild Flysch in the middle of the catchment and Waegitaler Flysch in the lower part of the catchment (Fig. 3b). The soils are umbric or mollic Gleysols (Schleppi et al., 1998). The spatial heterogeneity of the soil is related to both the topography of the site and the vegetation (Schleppi et al., 1998). Feyen et al. (1996) states that the shallow gleyic soils and the clay-rich sub-soils have a low permeability. However, the large number of stones, old tree roots and dead wood in the anoxic soil layers result in a continuous network of large pores (Feyen et al., 1996). Soil depth ranges from 0.5m at the ridge sites to more than 2.5m in depressions (Rinderer et al., 2014). Shallow soils (< 1m) occupy about 55 % of the catchment area (see dotted areas in Fig. 3b) and are present in all catchments.

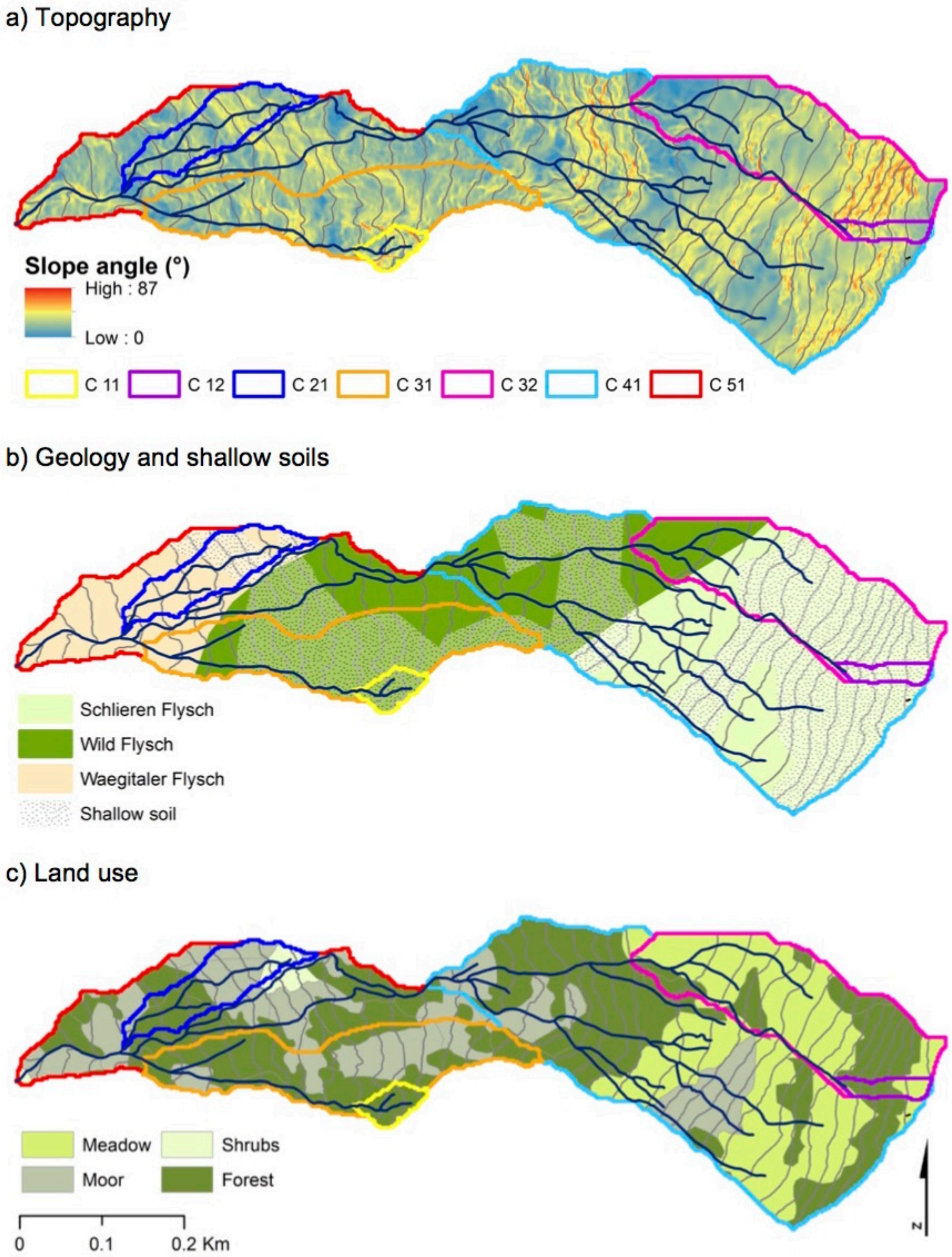


Figure 3: Maps of the Studibach catchment with a) topography: slope angle (°) and contour lines (every 10 m), b) geology: three types of flysch with dotted areas indicating shallow soils and c) land use: meadows, moors, shurbs and forests. Data source; topography: DEM; swissALTI3D; (Federal Office of Topography Swisstopo, Bern); geology: geologic map from Hantke (1967); land use: aerial photo (Spot Mosaic; Federal Office of Topography Swisstopo, Bern); wetlands: from the Federal inventory of wetlands of national importance (Swiss Federal Office for Environment, Bern).

In the upper catchment area, meadows and forests are the dominant land use types, while in the lower catchment areas, forests and moors are dominant. While catchment C12 is totally forested, all other catchments have forested areas at steeper parts and ridges, and open meadows at the flatter areas. The meadows in the upper part of the catchment are used for cattle grazing in the summer and hikers use the hiking paths. In the lower catchment areas, there is no human influence on the catchment apart from the walking pathes created by the researchers from the University, ETH and WSL.

Table 1: *Topography, geology and land use information for each subcatchment calculated in ArcMAP from the datasets shown in Fig. 3.*

			C 11	C 12	C 21	C 31	C 32	C 41	C 51
Topography	Area (ha)		0.3	0.2	1.1	3.2	3.8	12.5	20.6
	Altitude (m)	Min	1’388	1’593	1’307	1’311	1’497	1’421	1’270
		Mean	1’406	1’628	1’343	1’386	1’562	1’535	1’468
		Max	1’425	1’650	1’388	1’469	1’656	1’656	1’656
	Slope angle (°)	Min	2	7	4	1	0	0	0
		Mean	25	25	19	20	23	22	21
		Max	58	56	40	58	66	66	66
Geology	Waegitaler flysch (%)		0	0	100	10	0	0	16
	Wild flysch (%)		100	0	0	90	19	30	42
	Schlieren flysch (%)		0	100	0	0	81	70	42
	Shallow soils < 1m (%)		99	100	36	71	70	62	55
Land use	Meadow (wet) (%)		46	-	51	34	63	57	50
	Shrubs (%)		-	-	11	-	-	-	2
	Partly forested (%)		-	-	38	26	9	5	15
	Dense coniferous forest (%)		54	100	-	40	28	38	32

For this master thesis the sub-catchments C21 and C32 were selected for the stream water analysis. They differ in size and elevation but both are characterized by a heterogenous land use and small scale topography.

3 Methodology

In this chapter, the experimental setup of the Studibach catchment is explained, followed by the sampling strategy of the snapshot campaigns, sample treatment and laboratory analyses. Lastly, the set-up of the continuous salt tracer injection test is described.

3.1 Experimental setup

A total of 51 groundwater wells were installed in the seven sub-catchments of the Studibach catchment in 2010/2011 (Fig. 4). The well sites were chosen based on a stratified sampling procedure to cover the range of topographic positions, soil types and vegetation (Rinderer et al., 2015). This procedure resulted in groundwater measurements at 8 ridge sites, 22 midslope and 21 footslope or depression sites; 20 sites are forested and 31 sites are located in grassland. The well depth varies between 0.46 m and 2.16 m.

Continuous monitoring of the shallow groundwater levels occurred at a 5 minute interval from May – November using Odyssey capitance water level loggers (Dataflow Systems Pty Limited). In eight groundwater wells water level, electrical conductivity (EC) and temperature were recorded at a similar interval using Keller (DCX-22 CTD) and STS (DL/N 70, Sensor Technik Sirnach AG) sensors. At two locations in the catchment (1195 m a.s.l. and 1415 m a.s.l.) barometric pressure was measured to correct the pressure data for the influence of changes in the atmospheric pressure and to obtain the groundwater levels.

Stream levels were measured at 1 or 5 minute intervals during summer and pressure was measured using a Keller (DCX-22 CTD; in C21) or STS (DL/N 70, Sensor Technik Sirnach AG; in C32) sensor (depending on data storage possibilities). Manual water level measurements were conducted every 2 months during the summer, when the data was downloaded from the sensors. The subcatchments under study were equipped at a V-notch weir and monitored with a Keller (C 21) and STS (C 32) pressure transducer at the catchment outlet (Fig. 4).

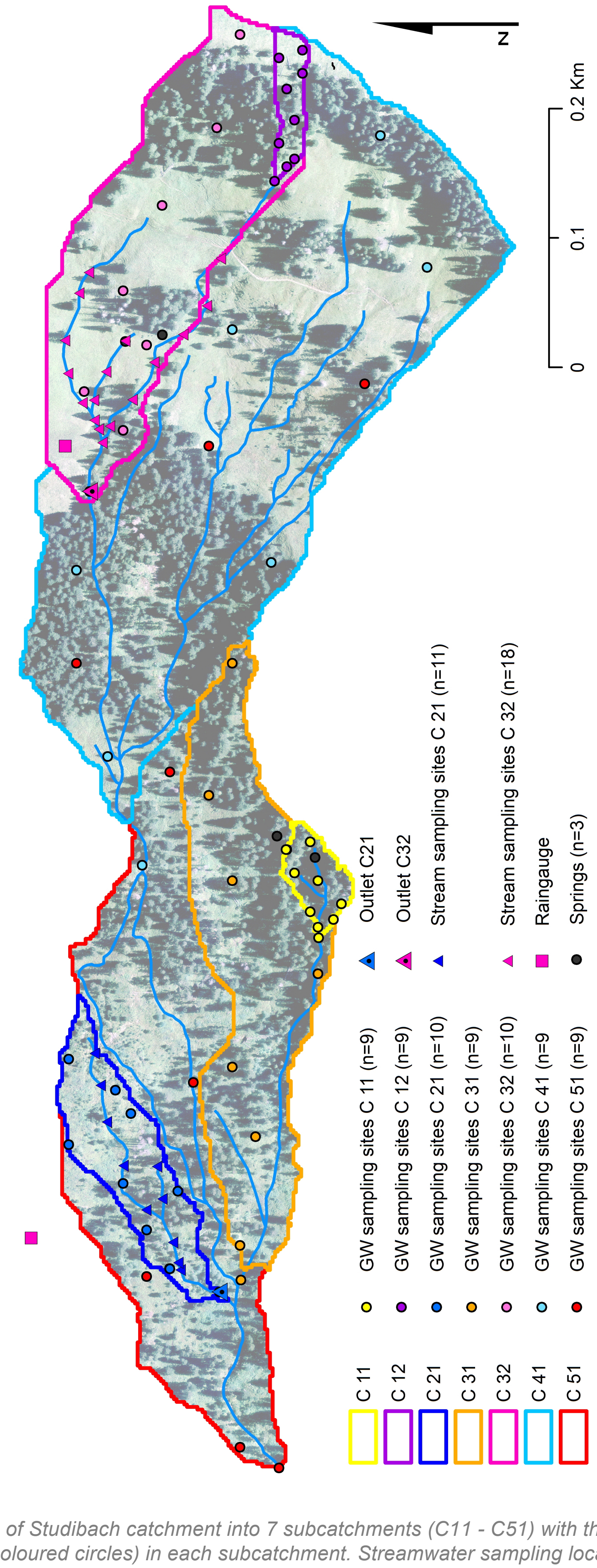


Figure 4: Subdivision of Studibach catchment into 7 subcatchments (C11 - C51) with the groundwater (GW) sampling locations (coloured circles) in each subcatchment. Streamwater sampling locations (triangles in C21 and C32). Springs (black circles) and raingauge (pink square) in C32.

Precipitation was measured at two locations (1’361 m a.s.l. and 1’502 m a.s.l.; Fig. 4) in the catchment using tipping bucket rain collectors (7852, Davis Instruments) connected to an Odyssey Rain Gauge logger (Dataflow Systems Pty Limited). Additional meteorological data is available from the nearby WSL climate station Erlenbach (1’220 m a.s.l., Swiss coordinate system: 697'000 / 210'950).

3.2 Methods

Data collection of groundwater and streamwater occurred through 4 snapshot sampling campaigns and 2 continuous salt tracer injection experiments in the two selected study sub-catchments C21 and C32.

3.2.1 Snapshot Sampling

To assess the variability in the chemical and isotopic composition of groundwater and streamwater, snapshot sampling campaigns were performed in the subcatchments. Prior to a sampling campaign the groundwater wells were purged to avoid the sampling of standing water. Sampling of stream or groundwater included measuring the electric conductivity (EC) and pH (WTW, GmbH) before the sample was taken. To avoid external influences (e.g. rain events), the sampling campaigns were carried out within one day. The individual streams were sampled from the outlet upwards to the source within the timeframe of 2 hours.

3.2.1.1 Sampling Strategy

The sampling sites along the streams were approximately 40 meters apart, marked with flags and the location was recorded with a GPS-device (Garmin eTrex30) to ensure that the samples were taken at the exact same location in the different sampling campaigns. Stream samples were only taken if there was observable flow (> 0.1 l/s). The 4 snapshot campaigns were performed with a monthly interval from July to November (Table 2). Small shifts in the time schedule were due to weather conditions and the availability of laboratory facilities. To capture baseflow conditions, there had to be little or no precipitation several days prior to the sampling date. However, for sampling campaigns 2 and 3, there was precipitation in the catchments within the previous 2 days (Fig. 5; Table 2). The catchments respond quickly to precipitation and therefore, streamflow had returned to baseflow during the sampling.

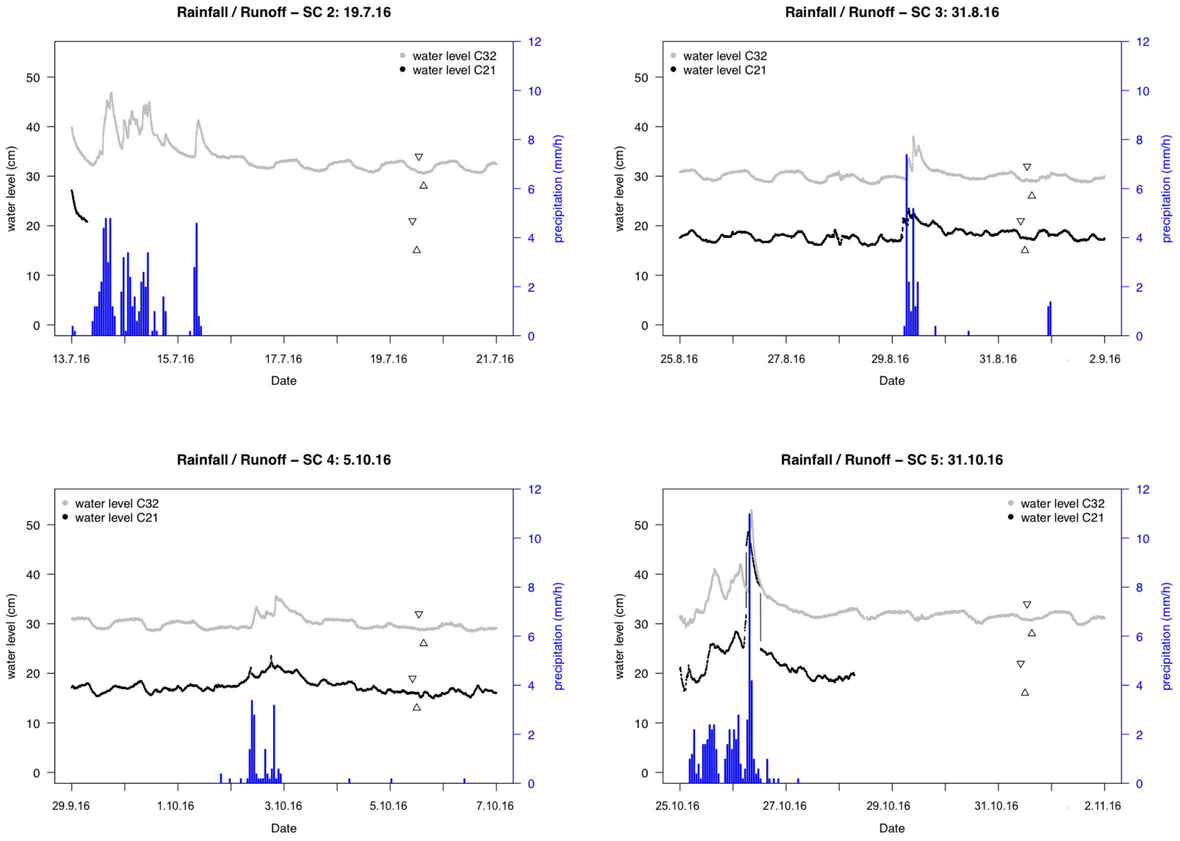


Figure 5: Rainfall / runoff situation per sampling campaign (SC2 - SC5). Water level at the outlet of C32 (grey) and water level at the outlet of C21 (black), rain in bars (blue). Triangles mark the beginning (∇) and end (Δ) of the sampling on the sampling day.

Table 2: API $_{7/5/2}$ and mean water level and overall catchment wetness (C32) at outlet during sampling per sampling campaign (SC2 – SC5).

					mean water level (cm) at outlet during sampling		overall catchment wetness; Q(l/s)
SC	Date	API7 (mm)	API5 (mm)	API2 (mm)	C21 (10:00 - 12:00)	C32 (13:00 - 15:00)	C32
SC2	19.07.16	100.0	33.4	0.0	-	37	1.96
SC3	31.08.16	20.2	20.2	20.2	17	29	1.67
SC4	05.10.16	17.0	16.8	0.2	16	29	0.32
SC5	31.10.16	56.0	30.2	0.0	-	38	1.4

3.2.1.2 Sample Collection

Stream water was collected by immersing the bottle into the stream, while groundwater was extracted from the wells with a syringe and tube. Both were rinsed before collecting the sample. The sample bottles (polyethylene, 50 – 300ml) were filled and air space was minimized to avoid post-sampling interactions. The samples were stored at relatively cool conditions until laboratory analysis at ETH Zürich, within 2 days of the sample collection.

3.2.1.3 Laboratory analysis

To avoid sample deterioration, the laboratory analysis was done within 48 hours after sample collection. The sample was filtered (0.45 μm, SimplepureTM Syringe Filter) and divided into three different vials for further analysis.

For the cation analysis, 15 mL polyethylene vials were filled with the filtered samples. These samples were acidified with 50 μl of 50mM HNO_3 to reduce precipitation and microbial activity and to preserve trace metals. The samples were analysed with a mass spectrometer (ICP-MS 7800, Agilent technologies, USA) at ETH Zürich, which was calibrated to 10 standards: six concentrations (0.1ppb, 0.5ppb, 1ppb, 5ppb, 10ppb and 25ppb) of the Multielement standard solution 5 for ICP (TraceCERT, SIGMA-ALDRICH), and four concentrations (1ppm, 10ppm, 50ppm and 100ppm) of the 1000ppm standards for Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}.

For the anion analysis, the filtered samples were put into 2 ml glass vials and closed with a 2-layered membrane cap or clamp cap. The samples were analysed with an ion chromatographer (861 Advanced Compact IC, Metrohm) and an autosampler (Spark, MIDAS). The measurements were calibrated to five standards: a 1:1, 1:2, 1:4, 1:10, and 1:20 dilution of Multi Anion Standard 1 for IC (TraceCERT, SIGMA-ALDRICH).

For the isotopic analysis, 20 ml of filtered sample was filled in a glass vial and closed with a screw cap. If there was not enough sample material available, it was filled into a 2 ml autosampler vial with a triple-septum screwing cap (BGB Analytik) because the analysis only requires ~1 ml of filtered sample. The samples were analysed with a Cavity Ring-Down Spectroscope Picarro L1102-I Liquid Analyser (1st generation analyser, Picarro Inc. 2008) at the University of Freiburg, Germany.

The collected data from the field and the laboratory was analysed in Excel, the statistical software RStudio (Version 1.0.44) and ESRI ArcMap.

3.2.2 Continuous salt tracer experiments

Two continuous salt tracer experiments were performed in the two catchments (Fig. 6; Table 3) by continuously injecting a salt brine (5 ml/s) into the stream using a mariotte bottle (Fig. 7), until a steady-state condition was reached. Pools and backwater areas in the stream section were avoided in order to minimize the time needed to reach steady state. The EC was measured every 5 meters along the stream using and EC meter (WTW, GmbH). Additional measurements were taken at special sections like a small waterfall (< 1 m) and before and after a tributary flowed into the stream.

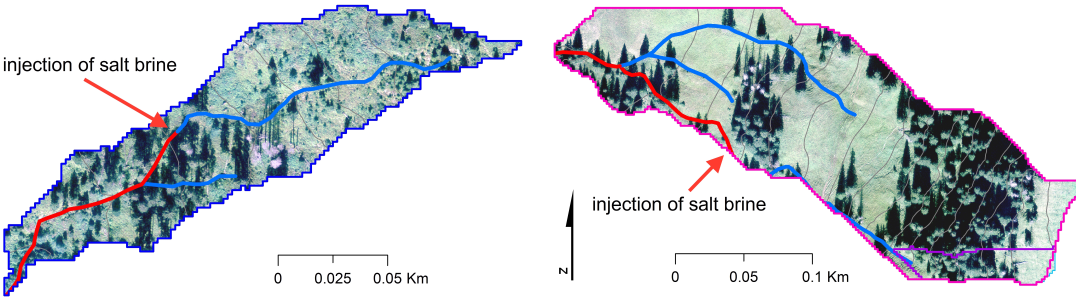


Figure 6: Stream sections (red), where salt tracer experiment was performed in C21 (left) and C32 (right).

Contributions to the stream discharge (e.g. inflow from groundwater or tributaries), increased the proportion of water compared to the salt in the stream and therefore decreased the stream EC. At the locations where a tributary flowed into main stream, the EC dropped instantly, while a constant inflow of groundwater or overland flow along the stream results in a gradual decrease in EC. To ensure the background EC of the stream was constant, it was monitored continuously during the experiment above the injection point.

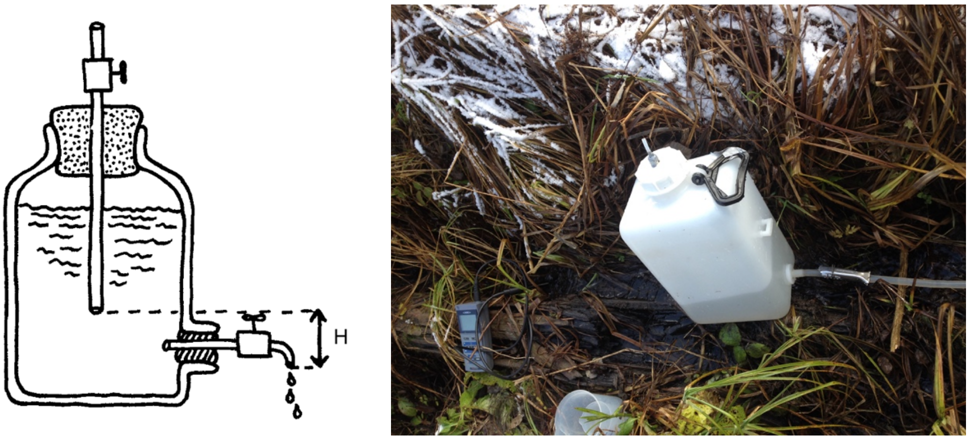


Figure 7: Schematic drawing of mariotte bottle (left: after the new Zealand digital library) equipped with an airtight cap. The only way for air to get into the bottle hast o be through the inlet tube. By moving the tube up or down, “H” is in- or decreased and the deliver rate is in- or decreased. The smaller “H”, the smaller the amount of solution flowing out of the bottle. Picture of mariotte bottle in use in Alptal (right).

Table 3:Technical data (date, time, background EC, API$_{7, 5, 2}$ and mean water level in C32 of continuous salt tracer experiments in C21 and C32.

	Date	Time	Background EC (µS/cm)	API7 (mm)	API5 (mm)	API2 (mm)	Runoff at injection of salt brine (ml/s)
Salt tracer experiment C32	29.09.16	12:00 - 19:00	356	11.0	10.8	6.2	200
Salt tracer experiment C21	03.11.16	11:00 - 15:00	313	1.4	1.2	1.2	300

4 Results

This chapter covers the results of the study. First, the observed stream water and groundwater chemistry is presented, with a specific focus on the spatial and temporal variability. Then, the results of the two continuous salt tracer experiments are presented. In the third part, the relation between the observed hydrochemistry and land use and topographic indices is explored. Lastly, the representativeness of measurements at the catchment outlet is investigated by comparison of the measurements at the outlet with the more detailed spatially distributed observations.

4.1 Spatial and temporal variability in streamwater chemistry

Research question 1: What is the spatial and temporal variability in the chemical and isotopic composition of groundwater and streamwater during baseflow conditions?

The spatio-temporal variability in EC, δ^2H, Ca^{2+} and Mg^{2+} is presented in Fig. 8 (C21) and Fig. 9 (C32). Measurements from sampling sites 21.02 and 21.03 in SC2 are missing (Fig. 8, C21) due to an error in the anion analysis in the laboratory.

A consistent fluctuation of the EC throughout all sampling campaigns was observed in C21 (Fig. 8). The EC always increased along stream branch 1, corresponding to observation site 21.12 and 21.11, decreased along stream branch 2 from site 21.25 to 21.21, and decreased further downstream from the confluence, from site 21.03 to the outlet (21.0). The highest EC was observed in SC3 and SC4.

δ^2H was roughly constant in branch 1, while δ^2H became less depleted along branch 2 (Fig. 8). Concentrations of Ca^{2+} decreased marginally or remained stable along branch 1, while along branch 2 the Ca^{2+} concentrations were stable or increased slightly from the top of the catchment towards the confluence with branch 1. Mg^{2+} concentrations were stable or decreased along branch 1. In branch 2, there were only minimal changes in the Mg^{2+} concentrations, and no clear pattern could be distinguished.

For all data presented above, EC, δ^2H and concentrations of Ca^{2+} and Mg^{2+} were higher in SC3 and SC4 compared to SC2 and SC5. In C21, the overall spatial variability was small with no sudden jumps in the observed hydrochemistry (Fig.8).

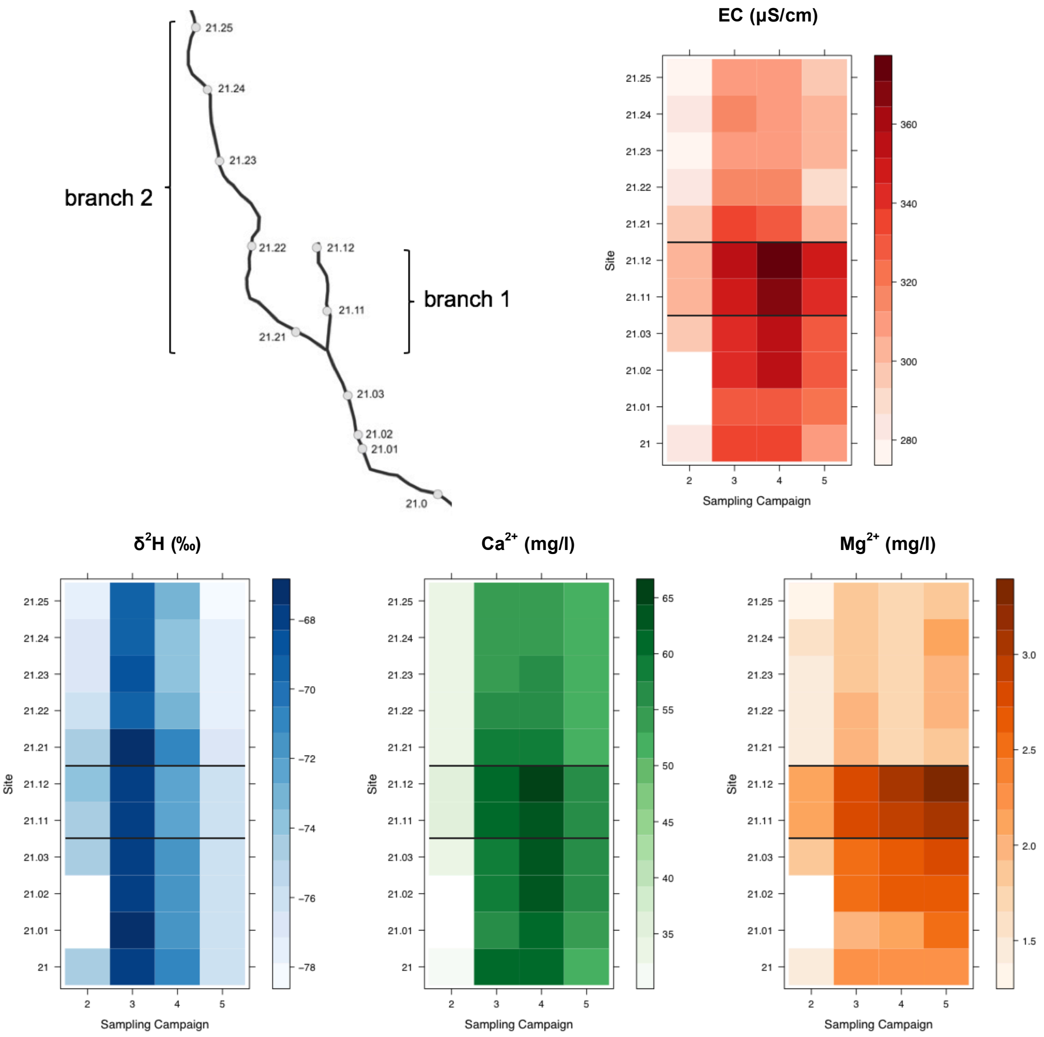


Figure 8: Heatmap showing the spatial and temporal variability of electrical conductivity in catchment 21. The EC values of the individual sites (rows, from the top of the stream (top) to the outlet (bottom)) are shown per sampling campaign (columns, SC 2-5). The black lines indicate the subdivision of different branches or sections.

In C32 the spatial variability in EC was was also consistent for the different sampling campaigns (Fig. 9). The EC decreased in branch 1, from the spring towards the confluence with branch 2, and in branch 2, from the top of the stream (32.25) towards the confluence (32.21). For all four sampling campaigns the EC along branch 3 decreased from site 32.36 to 32.34 and increased from site 32.34 to 32.33. After this increase, the EC decreased again towards the end of branch 3. At sampling locations 32.03 and 32.02, the stream water EC was relatively similar (273 ± 23 µS/cm) during the different sampling campaigns. Measurements from the sampling locations 32.01 until the catchment outlet (32.0) also had a consistent EC (310 ± 7 µS/cm) during the different sampling campaigns. δ^{2}H became less depleted or remained stable along branch 1. In the upper part of branch 2 (32.25 – 32.24) δ^{2}H was stable or became slightly less depleted, while from 32.23 towards 32.21 δ^{2}H became less depleted or remained stable (SC5). δ^{2}H in branch 3 showed no distinct pattern. In SC2, SC4 and SC5, the δ^{2}H got more negative between observation sites 32.34 and 32.33 and maintained this signature until the confluence with branches 1 and 2. In SC3, δ^2H became less depleted between 32.34 and 32.33 while they became more depleted towards the confluence with the other branches (Fig. 9).

Ca^{2+} concentrations increased along branch 1 in SC2, while a decrease in the Ca^{2+} concentrations was observed in all other sampling campaigns (Fig. 9). The Ca^{2+} concentrations in branch 2 decreased from the streamhead towards the confluence with branch 1. A drop in the Ca^{2+} concentrations was observed in all sampling campaigns between observation site 32.24 and 32.23 (59 ($Q_{mean(32.24)}$) to 42 mg/l ($Q_{mean(32.23)}$)). In branch 3 the Ca^{2+} concentrations did not change in SC3 and SC4, while in SC2 and SC5 Ca^{2+} concentration

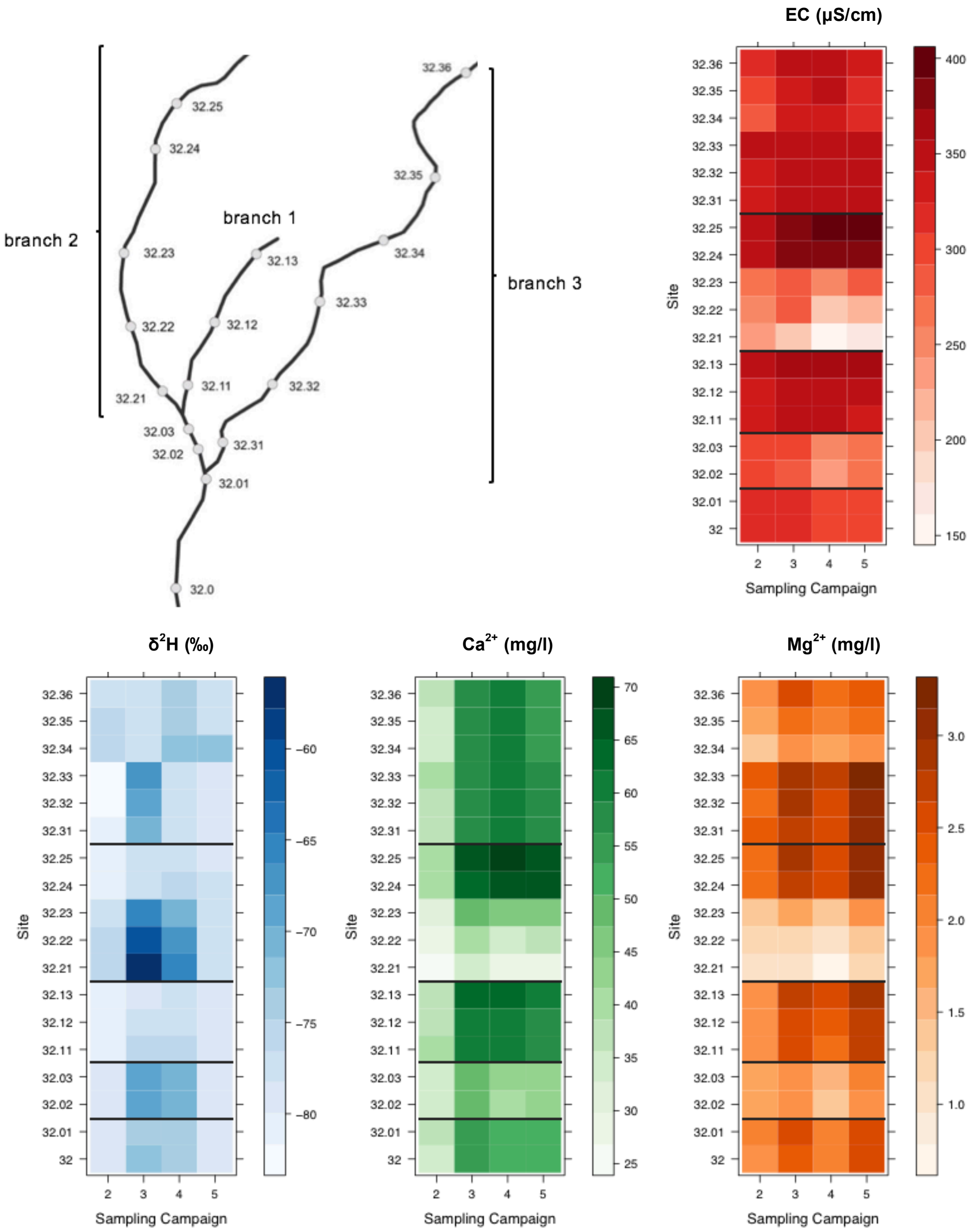


Figure 9: Heatmap showing the spatial and temporal variability of electrical conductivity in catchment 32. The EC values of the individual sites (rows, from the top of the stream (top) to the outlet (bottom)) are shown per sampling campaign (columns, SC 2-5). The black lines indicate the subdivision of different branches or sections.

increased between observation sites 32.34 and 32.33. Ca^{2+} concentrations decreased towards the junction with branch 1 and 2. Mg^{2+} concentrations in branch 1 were stable (SC2) but generally decreased along the stream. Stable or slightly decreasing Mg^{2+} concentrations were observed in the upper part of branch 2 until observation site 32.24 (Fig. 9). For all sampling campaigns Mg^{2+} concentrations decreased suddenly between site 32.24 and 32.23, while a more gradual decrease was observed towards the end of branch 2 (32.21). In branch 3, Mg^{2+} concentrations decreased in the upper stream zone (32.36 – 32.24), and increased between observation site 32.34 and 34.33. From there on, concentrations decreased slightly from observation site 32.33 to observation site 32.31 in SC3 – SC5, while there was a slight decrease followed by a slight increase observed in SC2. At two locations a sudden change in all presented hydrochemical components was observed (32.24 – 32.23 and 32.34 – 32.33).

In C32 as well as in C21, there was no clear seasonal pattern in streamwater chemistry. The EC, δ^2H, Ca^{2+} and Mg^{2+} concentrations were lower in SC2 than in the other campaigns. The least negative δ^2H values were observed in SC3 and SC4.

While the spatial patterns along the stream branches are similar in all SC, the measured concentrations still differ from SC to SC. The most pronounced spatial variability in EC, δ^2H and Ca^{2+} was observed in the October 5 sampling campaign (SC4). Therefore, the

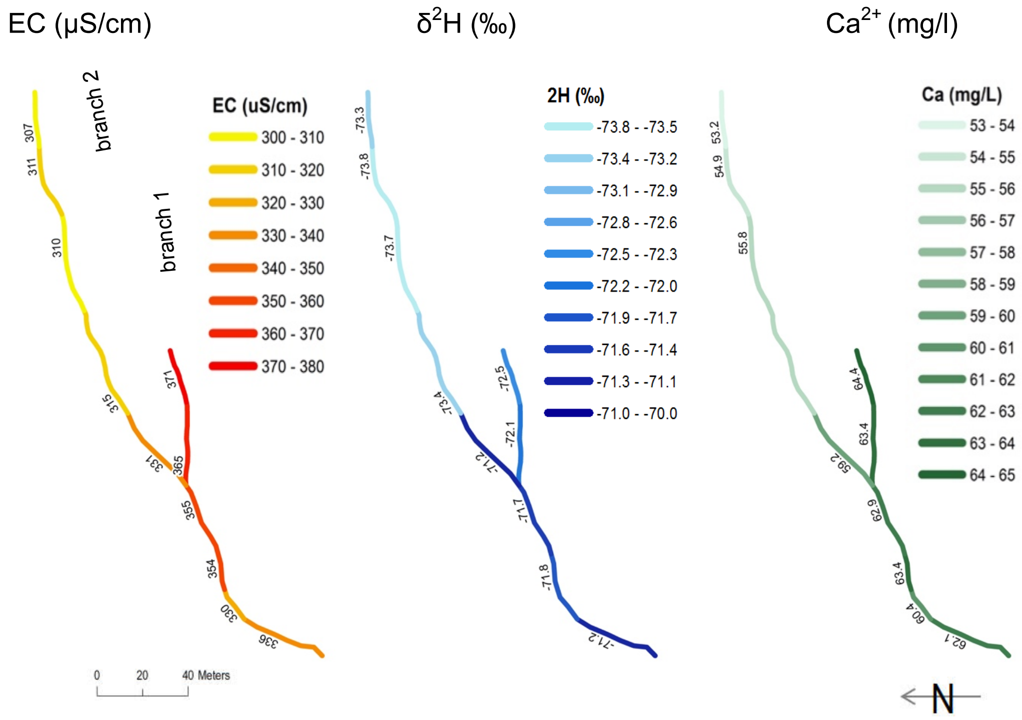


Figure 10: Spatial variability of EC, ^2H and Ca^{2+} of stream water in C21. Measured on October 5, 2016 (SC4). The observations are presented per sampling location for each stream section with a colour scheme, and the actual measurement values are shown next to each sampling location. The maps for all other sampling campaigns can be found in appendix B.

observations of this campaign are used to illustrate the observed spatial variability in hydrochemistry in more detail (Fig. 10; C21 and Fig. 11; C32). During this campaign the overall catchment wetness was lowest (see Table 2, Chapter 3.2.1.1).

The EC increased along branch 2 (C21), while in branch 1, the EC decreased from the upper part (371 to 365 μS/cm) to the confluence with branch 2 (Fig. 10: left). After the confluence, the EC continued to decrease down to 336 μS/cm. δ^2H was more depleted in the upper stream zone of branch 2 (δ^2H = -73.6 ‰), and got less depleted towards the confluence with branch 1 (Fig. 10: middle). In branch 2, the δ^2H also was less negative downstream. After the confluence of both branches, the δ^2H first showed a more depleted signature, and afterwards reached the most enriched δ^2H signature observed in the stream during this campaign (-72.47 ± 0,96‰). The Ca^{2+} concentrations slightly increased downstream along branch 2 (53.2 to 59.2 mg/l) from the start of the measurements to the inflow of branch 1 (Fig. 10: right). This is in contrast to branch 2, where the Ca^{2+} concentration slightly decreased downstream (64.4 to 63.4 mg/L). Downstream of the confluence of both branches, the Ca^{2+} concentration fluctuated a bit (±1.1 mg/l).

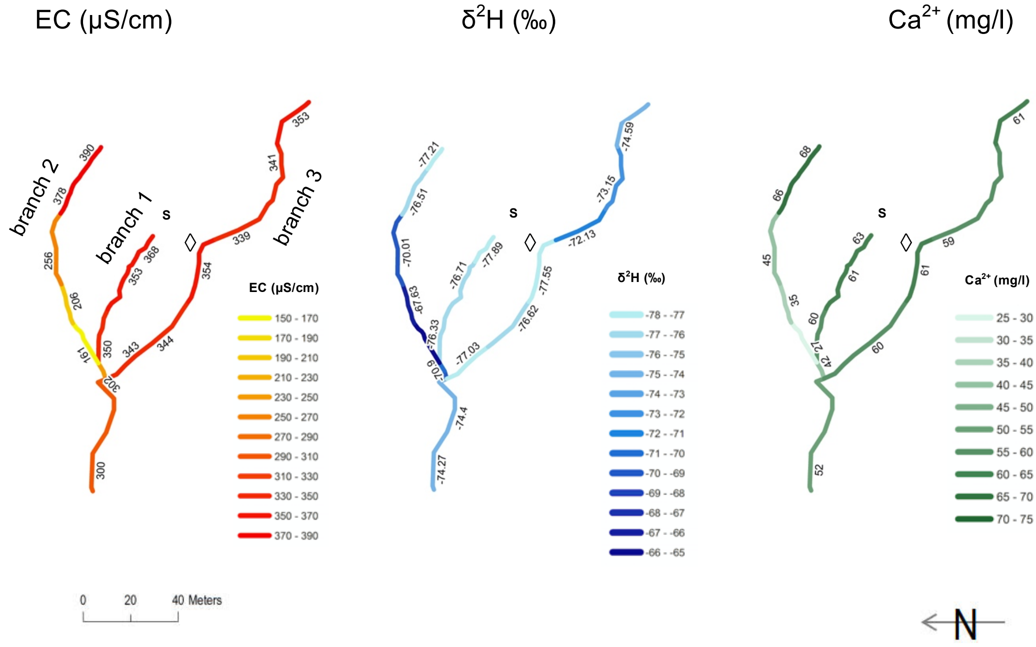


Figure 11: Spatial variability of EC, δ^2H and Ca^{2+} of stream water in C32 on October 5, 2016 (SC4). The observations are presented per sampling location for each stream section with a colour scheme, and the actual measurement values are shown next to each sampling location. The maps for all other sampling campaigns can be found in appendix B.

The EC, δ^2H and Ca^{2+} concentration in C32 on October 5, 2016 are shown in Fig. 11. In branch 2 (north), the EC decreased from the streamhead to the confluence with branch 1 (390 to 161 μS/cm). In branch 1, the EC decreased downstream from the perennial spring (Fig. 11: **s**) to the confluence (368 to 350 μS/cm).

In branch 3 (south), the EC fluctuated a bit, but overall variations were small (346 ± 6 µS/cm) until the confluence with the other two branches. The EC decreased slightly from the stream's origin (Fig. 11: s) to the marked (Fig. 11: ◊) bend in the stream (353 to 339 µS/cm), where the EC increased (339 to 354 µS/cm) preceding a decrease (to 343 µS/cm) towards the confluence with the other branches. Changes in δ^2H coincided with the observed changes in EC. δ^2H increased (i.e. showed a less depleted signature) along branch 2 (-77.21 to -70.9 ‰) and along stream branch 1 (-77.89 to -76.33 ‰). In branch 2 (south), the δ^2H became less depleted (-74.59 to -72.13 ‰) from the origin to the marked bend in the stream (Fig. 11: ◊), where δ^2H became suddenly more depleted (-72.13 to -77.55 ‰) and then remained relatively stable towards the confluence with the other branches. Ca^{2+} concentrations decreased more strongly along branch 2 (68 to 27 mg/l) than along branch 1 (63 to 60 mg/l). In branch 3, the Ca^{2+} concentrations remained relatively stable along the whole branch (± 2 mg/l) (Fig. 11).

The temporal variability in stream- and groundwater for EC, δ^2H and for the ions that had the largest variability (Ca^{2+}, Na^{+}, Mg^{2+}, Cl^{-}, SO$_4^{2-}$) is presented in the following boxplots (Fig. 12a-g). The variability between groundwater and streamwater was greater in C21 than in C32. Groundwater observations in C21 had a lower variability than observations of stream water chemistry, while in C32 the variability of groundwater and stream water tended to be more similar.

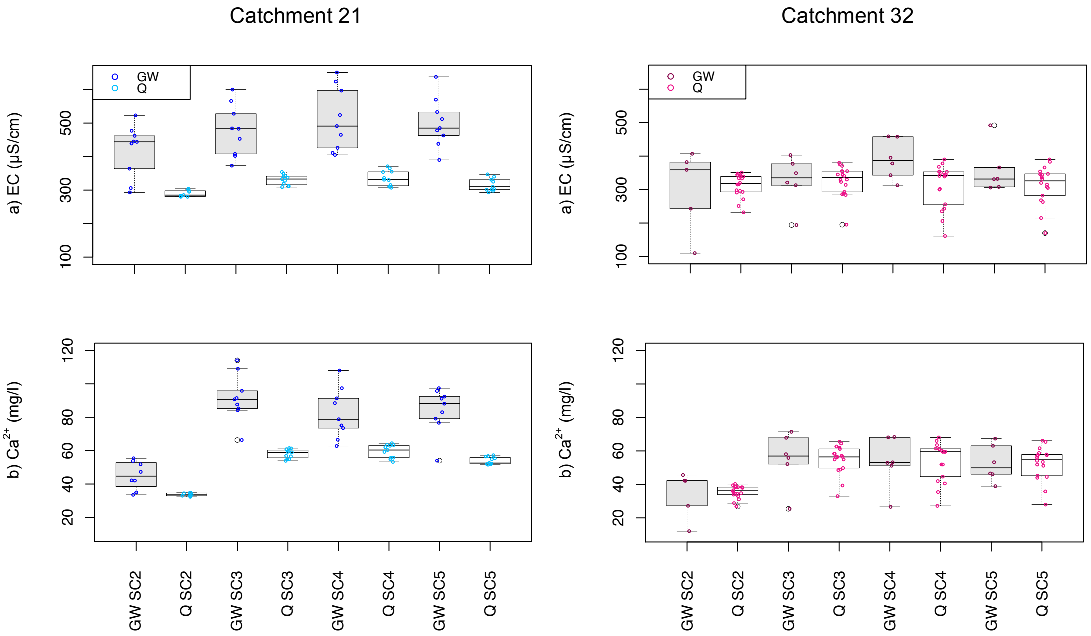


Figure 12: Boxplots of measured EC, cation (Ca^{2+}, Na^{+}, Mg^{2+}), anion (Cl^{-}, SO$_4^{2-}$) concentration and stable isotope (δ^2H) per water type (groundwater (GW), grey fill, dark blue (left) and deeppink (right) dots and stream water (Q), light blue (left) and pink (right) dots for each sampling campaign (SC 2-5) for catchment 21 (left) and catchment 32 (right). SC2 = 19.07.16, SC3 = 31.08.16, SC4 = 05.10.16, SC5 = 31.10.16.

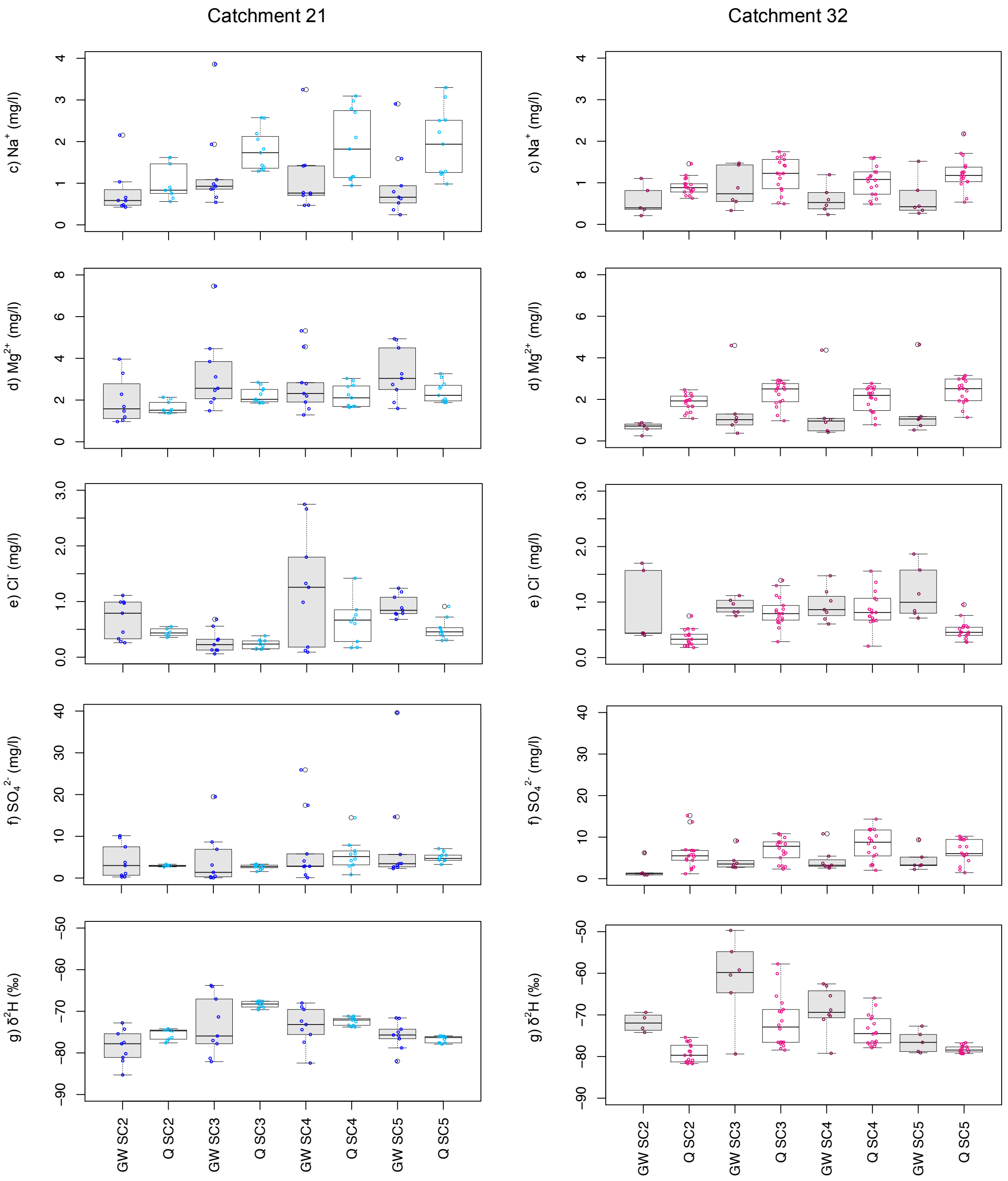


Figure 12f: Boxplots of measured EC, cation (Ca^{2+}, Na^+, Mg^{2+}), anion (Cl^-, SO_4^{2-}) concentration and stable isotope (δ^2H) per water type (groundwater (GW), grey fill, dark blue (left) and deeppink (right) dots and stream water (Q), light blue (left) and pink (right) dots for each sampling campaign (SC 2-5) for catchment 21 (left) and catchment 32 (right). SC2 = 19.07.16, SC3 = 31.08.16, SC4 = 05.10.16, SC5 = 31.10.16.

The results of the Kruskal-Wallis significance test ($\alpha = 0.05$), mean and standard deviation can be looked up in Table 7 and Table 8 in the appendix. Streamwater and groundwater in C21 were significantly different for EC, Ca^{2+}, Na^+, Cl^- and δ^2H (Table 4; Kruskal-Wallis significance test ($\alpha = 0.05$)). In C32, the groundwater EC, Mg^{2+}-, Na^+-, Cl^- and SO_4^{2-} concentrations and δ^2H were significantly different from streamwater concentrations. EC, Ca^{2+} and Na^+- concentrations of the groundwater were more similar to stream water in C32 than in C21. For Mg^{2+}, Cl^-, SO_4^{2-} and δ^2H an opposite pattern was observed: the groundwater- and stream water values were more similar in C21 than they were in C32.

Table 4: *Kruskal-Wallis significance test (α = 0.05), grey background indicates significant differences between groundwater and streamwater in the two sub-catchments.*

	Kruskal-Wallis p-value (α = 0.05)						
	EC	Ca^{2+}	Mg^{2+}	Na^{+}	Cl^{-}	SO_4^{2-}	δ^2H
C21 (GW vs. Q)	4.80E-12	2.53E-06	0.06	1.20E-05	0.05	0.34	0.05
C32 (GW vs. Q)	0.03	0.77	4.27E-07	2.61E-05	1.72E-04	1.14E-04	2.42E-04

To compare the two selected catchments, a Kruskal-Wallis significance test (α = 0.05) was performed on the observed EC and Ca^{2+}, Na^{+}, Mg^{2+}, Cl^{-}, SO_4^{2-} and δ^2H concentrations (Table 5). The EC, Ca^{2+}-, Na^{+}- and SO_4^{2-}-concentrations in the groundwater of C21 were significantly different from the groundwater in C32. Streamwater Na^{+} -, Mg^{2+} -, Cl^{-} -concentrations and δ^2H were also significantly different for the two catchments.

Table 5: *Kruskal-Wallis significance test (α = 0.05), grey background indicates significant differences between the two sub-catchments.*

	Kruskal-Wallis p-value (α = 0.05)						
	EC	Ca^{2+}	Mg^{2+}	Na^{+}	Cl^{-}	SO_4^{2-}	δ^2H
Groundwater (C21 vs. C32)	5.40E-11	1.85E-06	0.10	4.05E-03	0.98	2.74E-03	0.99
Streamwater (C21 vs. C32)	0.65	0.16	0.01	2.33E-09	1.88E-04	0.06	0.02

4.2 Groundwater source areas

Research question 2: What are the groundwater source areas that contribute to baseflow? Where does groundwater flow into the stream?

The spatial patterns in stream chemistry (chapter 4.1) were complemented with a continuous salt tracer experiment to identify where, and how much water flowed into the streams.

In C21, the background stream EC was 314 µS/cm. By injecting the salt brine, the EC was increased, to a maximum of 1'650 µS/cm (Fig. 13). Downstream of the initial mixing zone (0-10m) the stream EC decreased consistently (15 µS/cm per meter) for the next 30 meters (10m – 40m). Between 40 until 55 meter below the injection point, the EC remained constant. At 55 meters the EC dropped from 1050 to 900 µS/cm; at ~ 90 meters there was another abrupt decrease in EC (from 900 to 800 µS/cm). From there on until the outlet (125 meters after the starting point) the EC decreased only marginally. The decrease in EC at 55 and 90m distance coincided with the inflow of the second branch (at 55m) and a small inflow further downstream (at 90m). In between these inflows and in the last stream section (90-125m), no major changes in EC were observed. The first stream section (10-40m), where EC decreased steadily about 20 µS/cm per meter was much steeper than the 50-125m stream section, where only a slight dilution of the stream water was observed (Fig. 13). This suggests that groundwater entered the stream in the steep part while there was little contribution from groundwater to streamwater in the flatter part.

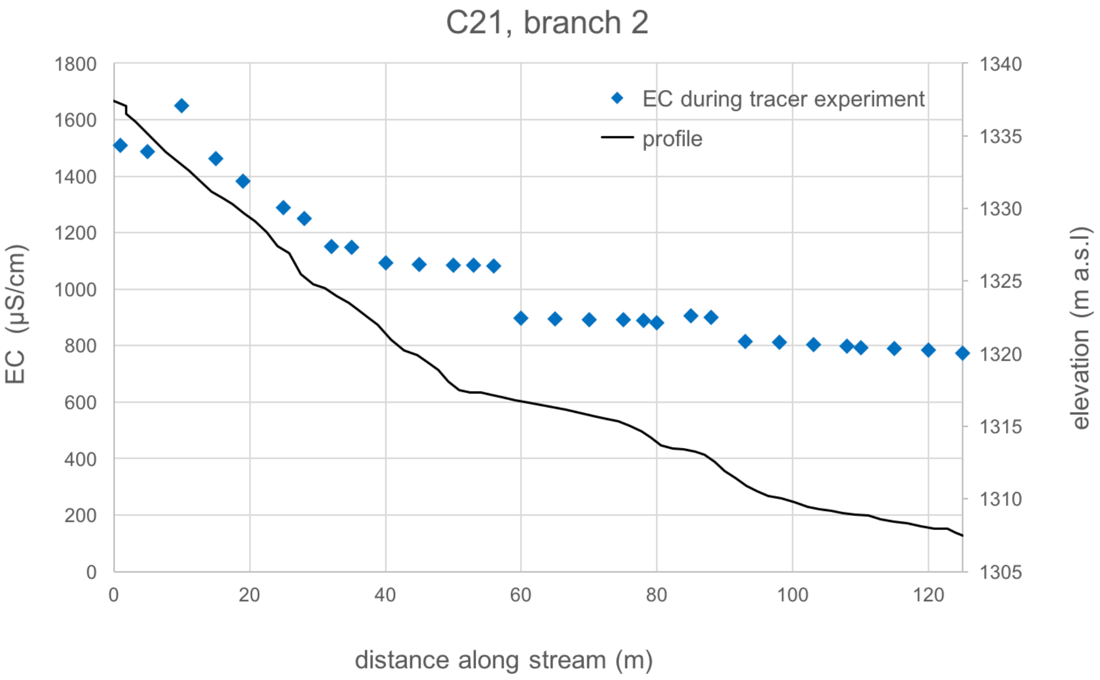


Figure 13: EC along the streamprofile during the continuous salt tracer measurement in C21, branch 2.

In order to estimate the groundwater contribution to the stream in the steep section, the mass balance assumption was used to determine the groundwater inflow (*X*);

$$C_{START} \times Q + C_{GW} \times X \; = \; C_{END}(Q + X)$$

$C_{START} = EC\ after\ salt\ brine\ injection\ to\ stream\ (\mu S/cm)$

$Q = Runoff\ at\ injection\ site\ (ml/s)$

$C_{GW} = mean\ EC\ of\ nearest\ groundwater\ source\ in\ all\ SC\ (\mu S/cm)$

$C_{END} = EC\ at\ end\ of\ stream\ section\ (\mu S/cm)$

$X = inflow\ per\ stream\ section\ (ml/s)$

where C_{START} and Q are the EC and the flow of the stream at the start of the stream section, C_{GW} is the EC of the groundwater source and C_{END} is the EC at the end of the stream section. This leads to the calculation for branch 2, C21:

$$1'400\frac{\mu S}{cm} \times 300\frac{ml}{s} + 550\frac{\mu S}{cm} \times X \; = 1150\frac{\mu S}{cm} \times \left(300\frac{ml}{s} \times X\right)$$

$$420'000 + 550\,X = 345'000 + 1150\,X$$

$$X \; \approx \; 125\frac{ml}{s} \; (in\ 20\ m\ stream\ section)$$

According to these assumptions and the above calculation, 125 ml/s were flowing from groundwater into the stream in the ~ 20 meters of steep stream section and gradually decreasing EC (=25 ml/s/m).

The experiment in C32 was conducted at branch 3 (most southern branch), which, during the experiment, had a discharge of ~ 200 ml/s, and a background EC of 356 µS/cm (Fig. 14). The EC reached a maximum of 950 µS/cm. Between 20 and 65 meters, i.e. the first section after the initial mixing zone, the EC decreased from 900 µS/cm to 650 µS/cm (5.5 µS/cm per meter) but from 65 to 100m the EC decreased only slightly. At 100m, where the confluence with the other stream branches in C32 happens, the EC dropped abruptly from 600 µS/cm to just under 500 µS/cm. In the last measured stream section (100 to 125 meters) the EC decreased only slightly (Fig. 14). A comparison of the measured EC with stream topography shows that (similar to C21) the continuous decrease in EC (20-65m

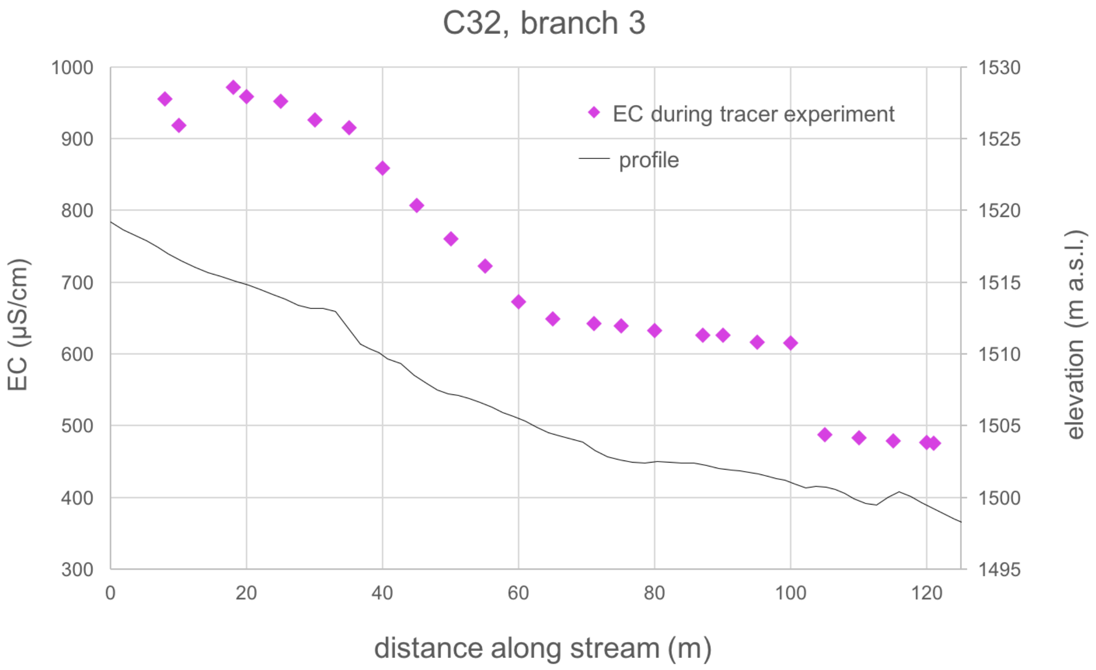


Figure 14: EC along the stream profile during the continuous salt tracer measurement in C32, branch 3.

after the injection point) occurred in a steeper stream section, while in the flatter section (65-125m only small changes in EC were observed.

The estimation of groundwater contribution in the steep stream section of C32 was calculated as in C21, above;

$$C_{START} \times Q + C_{GW} \times X = C_{END}(Q + X)$$

$$900\,\frac{\mu S}{cm} \times 200\,\frac{ml}{s} + 300\,\frac{\mu S}{cm} \times X = 650\,\frac{\mu S}{cm} \times \left(300\,\frac{ml}{s} \times X\right)$$

$$180'000 + 300\,X = 170'000 + 650\,X$$

$$X \approx 30\,\frac{ml}{s}\ (in\ 30\ m\ stream\ section)$$

Thus, ~ 30 ml/s were flowing from groundwater to streamwater in the 30 meters of steep slopes (= 1 ml/s/m), where EC decreased gradually. This is a much lower amount of groundwater contributing to the stream while the experiment was performed than in C21 (25 ml/s/m).

4.3 Topography and land use

Research question 3: Is the variability in the isotopic and chemical composition of streamflow related to topography or land-use?

4.3.1 Topography

In both catchments, the continuous salt tracer injection experiment showed a stronger dilution of the streamwater in the steeper stream sections. This suggests that topography affects the location of groundwater inflow to the stream and thus likely also affects the stream chemistry. Figure 15 shows the relation between EC and the calcium concentrations in the streamwater for steep slope sampling locations (>10° slope), and gentle slope sampling locations (<10° slope).

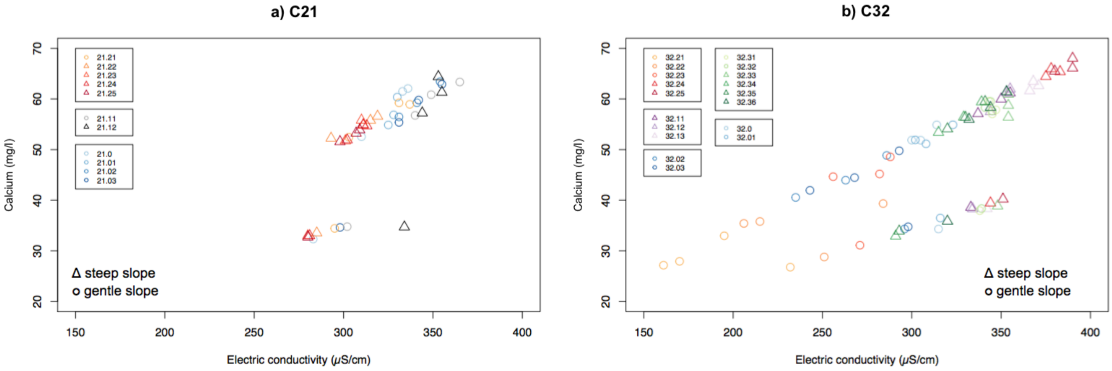


Figure 15: Calcium against EC measured in the two catchments C21 (a) and C32 (b). Different colours represent the different stream branches (one legend box per stream branch/section). Stream samples from steep sampling locations are presented by triangles and those in gentle slope areas by circles.

In C21 steep sampling locations had generally lower Ca^{2+} concentrations and a lower EC than gentle slope locations. Samples taken at location 21.12 (indicated in black in Fig. 15a) however, showed a different behaviour. However in C32, samples taken at steep slopes had higher Ca^{2+} concentrations and higher EC compared to the samples taken from gentle slopes. A comparison of the two catchments showed that the variability in both EC and Ca^{2+} concentrations was smaller in C21 than in C32. The Ca^{2+} concentrations and EC of the samples from the steep slopes in C21 and in C32 were similar. Ca^{2+} concentrations and EC at gentle slopes in C21 were generally higher than the measured EC and Ca^{2+} concentrations at gentle slope locations in C32.

Further comparison of EC, Ca^{2+}, Na^{+}, Mg^{2+}, Cl^{-} and SO_4^{2-}concentrations and δ^2H in steep an gentle slopes are presented in Fig. 16 a-g (Kruskal-Wallis significance test (alpha=0.05), mean and SD in Table 9 and Table 10 in the appendix).

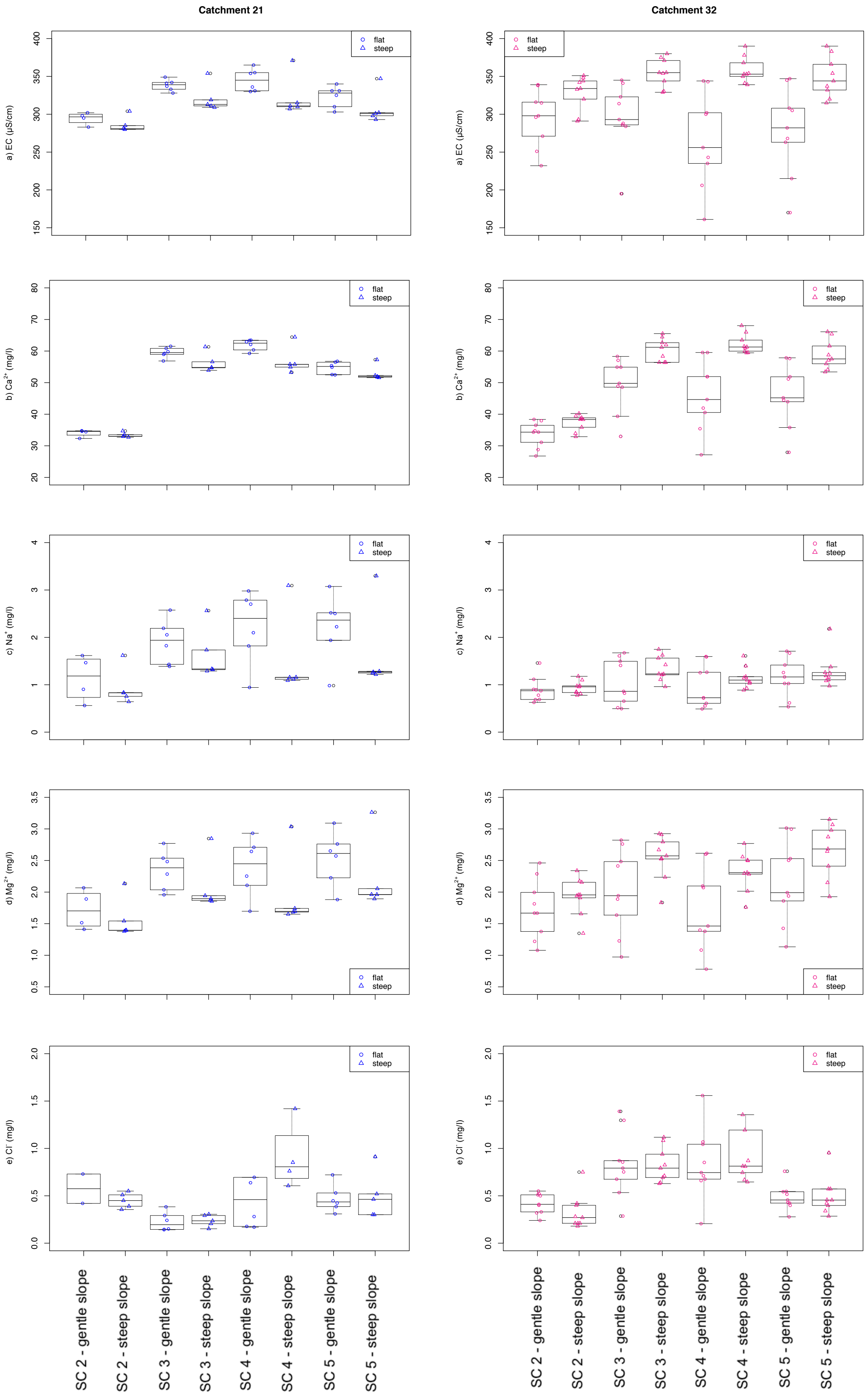


Figure 16: Boxplots of measured EC, cation (Ca^{2+}, Na^{+}, Mg^{2+}) and anion (Cl^{-}, SO_4^{2-}) concentrations and δ^2H in gentle and steep sampling sites per sampling campaign (SC 2-5) for both catchments (C21 and C32). SC2 = 19.07.16, SC3 = 31.08.16, SC4 = 05.10.16, SC5 = 31.10.16. → AXIS both pages

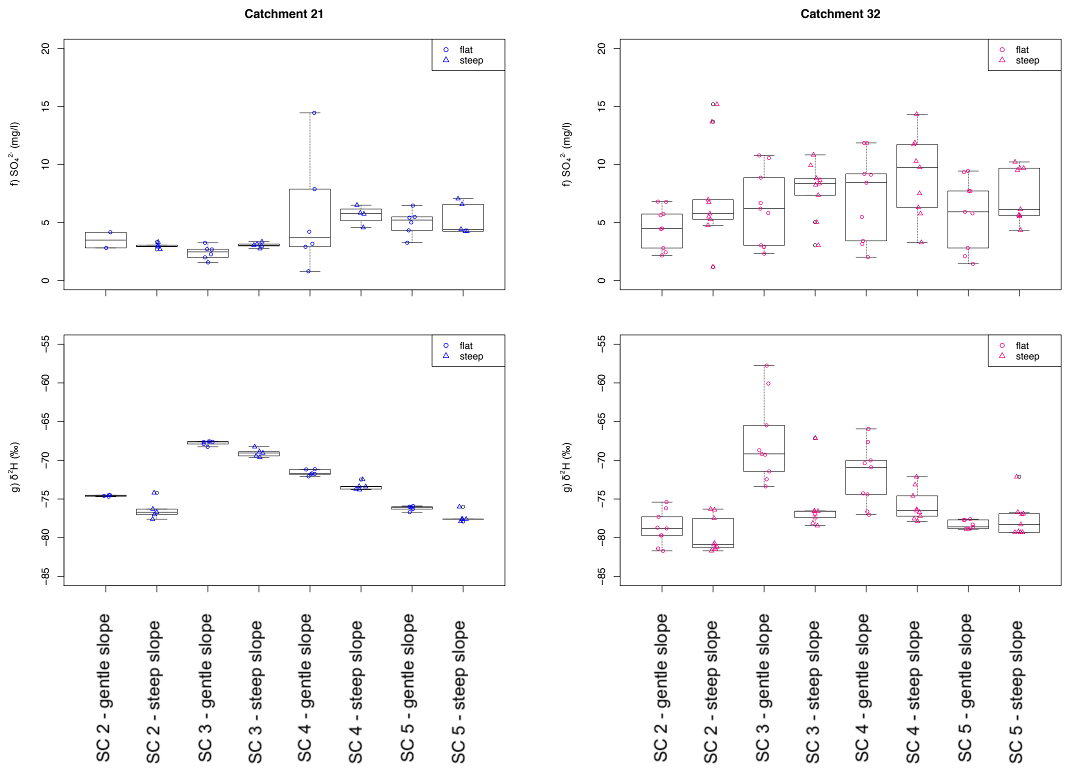


Figure 16f: Boxplots of measured EC, cation (Ca^{2+}, Na^+, Mg^{2+}) and anion (Cl^-, SO_4^{2-}) concentrations and δ^2H in gentle and steep sampling sites per sampling campaign (SC 2-5) for both catchments (C21 and C32). SC2 = 19.07.16, SC3 = 31.08.16, SC4 = 05.10.16, SC5 = 31.10.16. → AXIS both pages

The EC in C21 was significantly different in gentle slope stream sections than in steep stream sections (Fig. 16a). During the entire measurement period the EC was lower and less variable in steep sampling locations. Location 21.12, the origin of stream branch 1 in C21, was an outlier among the steep sampling locations, having a consistently higher EC and Ca^{2+}, Na^+ and Mg^{2+} concentration. In C32, EC was significantly lower and showed greater variability in gentle slope stream sections than in steep sampling locations during all snapshot campaigns. In C21, Ca^{2+}-concentrations at steep sampling locations were generally lower in SC3-SC5 and were less variable in SC2, SC4 and SC5 (Fig. 16b). In SC2, Ca^{2+}-concentrations at steep sampling sites were comparable to concentrations at gentle slope sampling sites and significantly lower than the Ca^{2+}-concentrations during the other campaigns. In C32, Ca^{2+}-concentrations at steep sampling locations were significantly higher in SC3 – SC5 than at the gentle slope stream sections, while in SC2, Ca^{2+}-concentrations were more comparable to the gentle slope stream sections. EC and Ca^{2+}-concentrations had a consistently smaller variability at steep sampling sites. In C21, Na^+-concentrations at steep sampling locations were generally lower and less variable than measurements from gentle slope sampling locations (Fig. 16c). In C32, the Na^+-concentrations from gentle- and steep sampling locations were similar in all campaigns but Na^+-concentrations at the steep sampling locations were less variable. In C21, Mg^{2+}-

concentrations from steep sampling locations had a smaller variability and were generally lower than concentrations from gentle slope sampling sites in all campaigns (Fig. 16d). In C32, Mg^{2+}-concentrations measured at steep sampling locations were slightly higher than concentrations measured at gentle slope sampling sites. The variability of Mg^{2+}-concentrations at steep locations was lower than at gentle slope sampling locations. In C21 and C32, there were no significant differences in Cl^{-}-concentration between gentle- and steep slope sampling locations (Fig. 16e). In SC4, the Cl^{-}-concentrations at steep locations were higher than at gentle slope sampling locations. In C32, Cl^{-}-concentrations were comparable in all SC. In C21, there was a significant difference in SO_4^{2-}-concentrations between gentle slope and steep sampling locations in SC3 (Fig. 16f). Noteworthy is also the large variability in SO_4^{2-}-concentrations at gentle slope sampling locations in SC4. In C32, SO_4^{2-}-concentrations were highly variable during all measurement campaigns. There were no significant differences in SO_4^{2-}-concentrations between gentle- and steep slope locations during all sampling campaigns. In C21, δ^2H was significantly more depleted in steep than in gentle slope locations in SC3 and SC4 (Fig. 16g). Remarkable is the very low variability of δ^2H within each campaign in C21, while in C32 the within-campaign variability of δ^2H is much larger. The δ^2H of gentle slope locations and steep locations was significantly different only in SC3 and SC4.

4.3.1 Land use

To analyse the relation between the variability in stream water chemistry and land use, the variability of EC, Ca^{2+}, Na^{+} and δ^2H was compared to the land use adjacent to the stream (Fig. 18 - Fig. 20; a-d). For better orientation, both catchments are depicted with their land use and an orthophoto in the background in order to see single treegroups as well (Fig. 17).

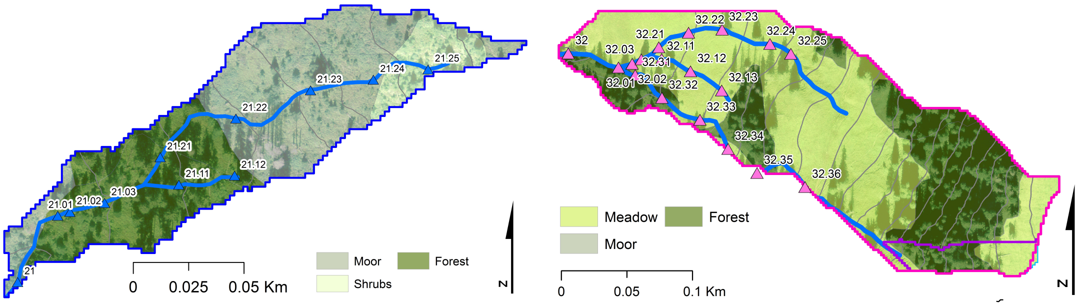
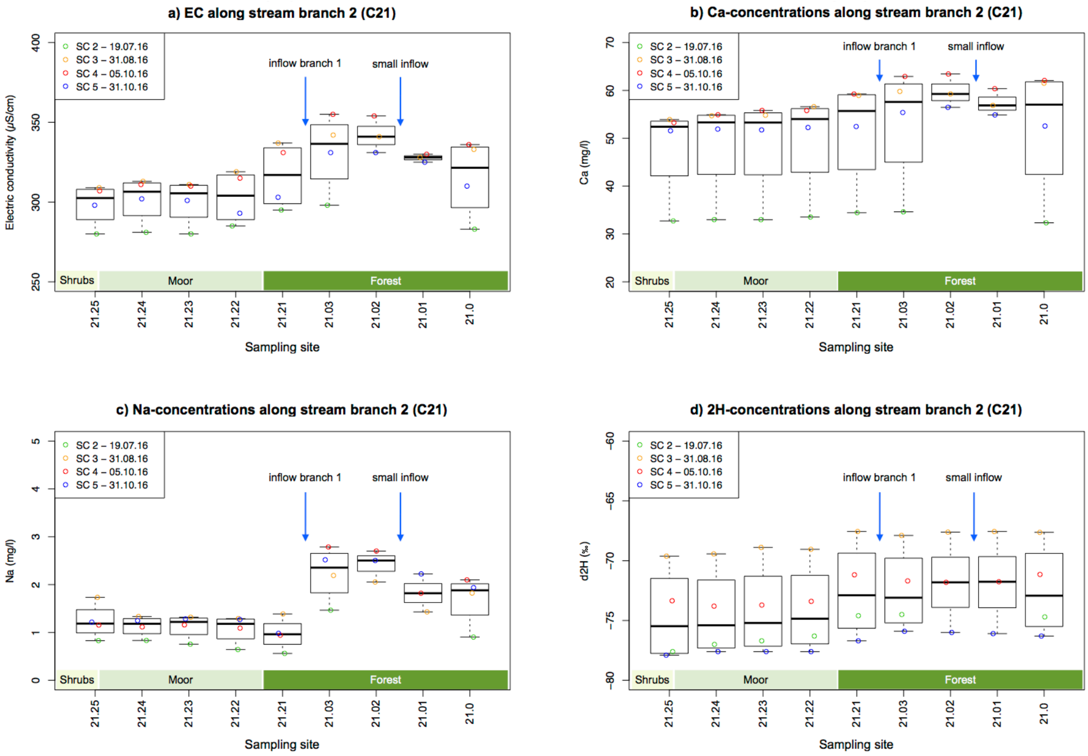


Figure 17: C21 (left) and C32 (right) with land use and orthophoto in the background.

In C21, the EC did not change along stream branch 2 from sampling locations 21.25 to 21.22, where the stream flows from an area with shrubs to a moor area (Fig. 18a). Between sampling locations 21.22 and 21.21, the stream flows from a moor into forest area and the EC increased. Another increase in EC was observed after the confluence with branch 1 and a major decrease was observed after a small inflow from a nearby moor / wet land, north from sampling locations 21.02 and 21.01 (Fig. 17, left). Ca^{2+}-concentrations increased along the stream branch, independent of land-use changes or the confluence with branch 1 (21.25 to 21.02; Fig. 18b). A decrease in Ca^{2+}-concentrations was observed at the second small inflow. Na^{+}-concentrations were relatively constant or decreased slightly along stream branch 2 (21.25 – 21.21) during all sampling campaigns; no major changes in concentrations were observed at changes in land use (Fig. 18c). After the confluence with stream branch 1, significantly higher Na^{+}-concentrations were measured during all campaigns and after the second, small inflow, a decrease in the Na^{+} concentration was observed. δ^2H was relatively constant along


a) EC along stream branch 2 (C21)

b) Ca-concentrations along stream branch 2 (C21)

c) Na-concentrations along stream branch 2 (C21)

d) 2H-concentrations along stream branch 2 (C21)

Figure 18: Land use compared to a) EC (µS/cm), b) Ca^{2+}-concentration (mg/l), c) Na^{+}-concentration (mg/l) and d) δ^2H (‰) from each sampling campaign (SC2 = 19.07.16, SC3 = 31.08.16, SC4 = 05.10.16, SC5 = 31.10.16) along branch 2 (C21). The lower bar in each subplot indicates the land use.

stream branch 2, in the shrub-covered- and the moor area (21.25 – 21.22), while δ^2H became slightly less depleted between sampling sites 21.21 and 21.03, where the stream enters the forest and remained relatively stable for the rest of the stream section (Fig. 18d).

In catchment 32, the different stream branches are almost exclusively surrounded meadows, although there are some land-use differences close to the stream (Fig. 17, right). EC was constant or slightly decreasing for EC, Ca^{2+}, Na^{+} and $\delta^{2}H$ at the first 2 sampling locations (32.25, 32.24; Fig. 19a-d). Between sampling site 32.24 and 32.23, the stream flows along some trees and shrubs, after which EC, Ca^{2+} and Na^{+} concentrations decreased and generally less depleted $\delta^{2}H$ was observed for all sampling campaigns (Fig. 4.19a-d). Further major changes in EC, Ca^{2+}, Na^{+} and $\delta^{2}H$ were only observed after the confluences with branch 1 and branch 3.

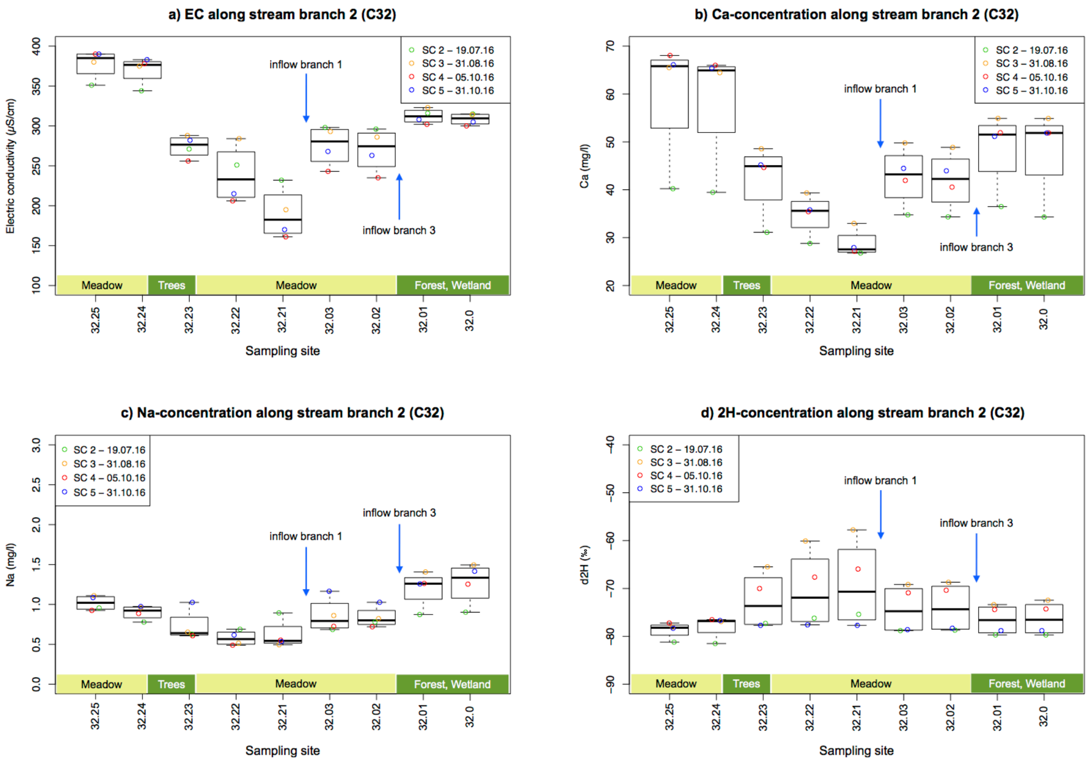


Figure 19: Land use compared to a) EC (µS/cm), b) Ca^{2+}-concentration (mg/l), c) Na^{+}-concentration (mg/l) and d) $\delta^{2}H$ (‰) from each sampling campaign (SC2 = 19.07.16, SC3 = 31.08.16, SC4 = 05.10.16, SC5 = 31.10.16) along branch 2 (C32). The lower bar in each subplot indicates the land use.

Stream branch 3 in C32, flows through meadows in the upper stream zone, through a forested area between sampling sites 32.32 and 32.31, and alongside a wetland with trees and shrubs at the last 2 sampling locations (32.01, 32.0). The EC, Ca^{2+}- and Na^{+}-concentrations and $\delta^{2}H$ for the adjacent land use zones are shown in Fig. 20a-d. Major changes in EC, Ca^{2+}- and Na^{+}-concentrations and $\delta^{2}H$ were observed in all sampling campaigns between sampling locations 32.24 and 32.23 and between 32.31 and 32.01. Sampling sites 32.34 and 32.33 are both located in the meadow and the major changes observed between 32.31 and 32.01 coincide with the confluence of stream branch 3 and the other branches (Fig. 20a-d).

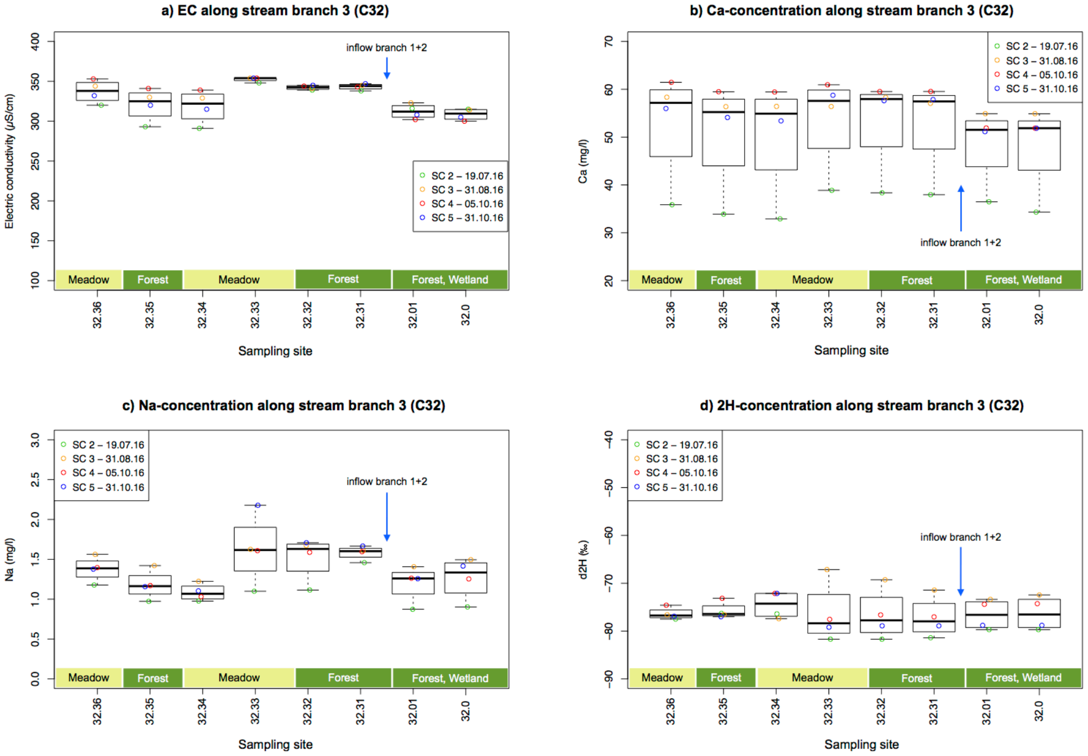


Figure 20: Land use compared to a) EC (µS/cm), b) Ca^{2+}-concentration (mg/l), c) Na^{+}-concentration (mg/l) and d) δ^{2}H (‰) from each sampling campaign (SC2 = 19.07.16, SC3 = 31.08.16, SC4 = 05.10.16, SC5 = 31.10.16) along branch 3 (C32). The lower bar in each subplot indicates the land use.

4.4 Representativeness of catchment outlet

Research question 4: Are measurements at the outlet of a catchment representative of the entire catchment?

The EC at the outlet of C21 was for all SC close to the median EC of all stream samples (Fig. 21a, left). In C32, the EC at the outlet was only close to the median EC of all stream samples for SC2, while for the other SCs, the EC at the outlet was lower than the median but still within the lower quartile (Fig. 21a, right). Ca^{2+} concentrations measured at the outlet of C21 were close to the median of all stream samples only for SC5. In SC4, concentration at the outlet was in the upper quartile and in SC2 and SC3, it was the upper (SC3) and the lower (SC2) extreme (Fig. 21b, left). In C32, Ca^{2+} concentrations measured at the outlet were within the lower quartile for all SC (Fig. 21b, right). For the other measured cations (Na^+ and Mg^{2+}; Boxplots in Fig. 26 in appendix) the concentrations at the outlet were within the upper and lower quartiles, except for the Na^+ concentration in SC5.

The Cl^- concentration at the outlet was close to the median of all samples in SC3 and SC4 in C21 and in SC5 in C32 (Fig. 21c). In C21, the measured outlet Cl^- concentration was the upper extreme value in SC5 and an outlier in SC2. In C32, Cl^- concentration measured at the outlet was just higher than the upper quartile in SC2 and was the lower extreme concentration in SC3 and SC4. SO_4^{2-} concentration (Fig. 26, in appendix) showed a similar pattern as outlet concentrations were also registered as lower extremes (C21 and C32, SC4) and also as an outlier (C21, SC2). δ^2H measured at the catchment outlet of C21 was

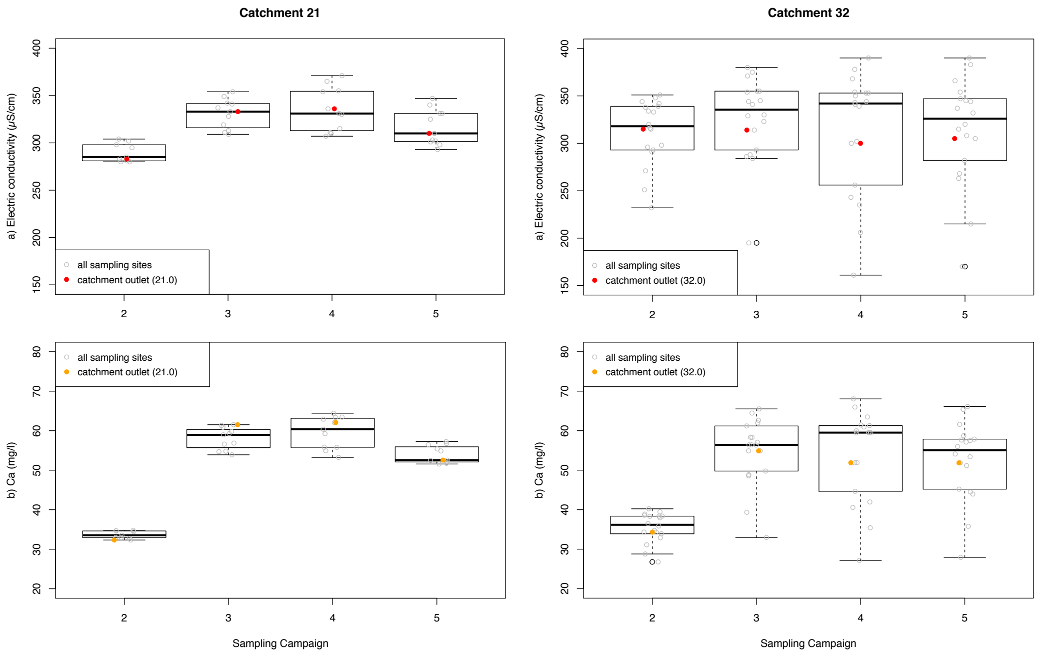


Figure 21: Boxplots of EC (a), Ca^{2+} (b), Cl^- (c), and δ^2H (d) of all stream sampling sites (grey circles) and the measurement at the outlet (coloured dots) of the catchments (C21: left and C32: right) per SC.

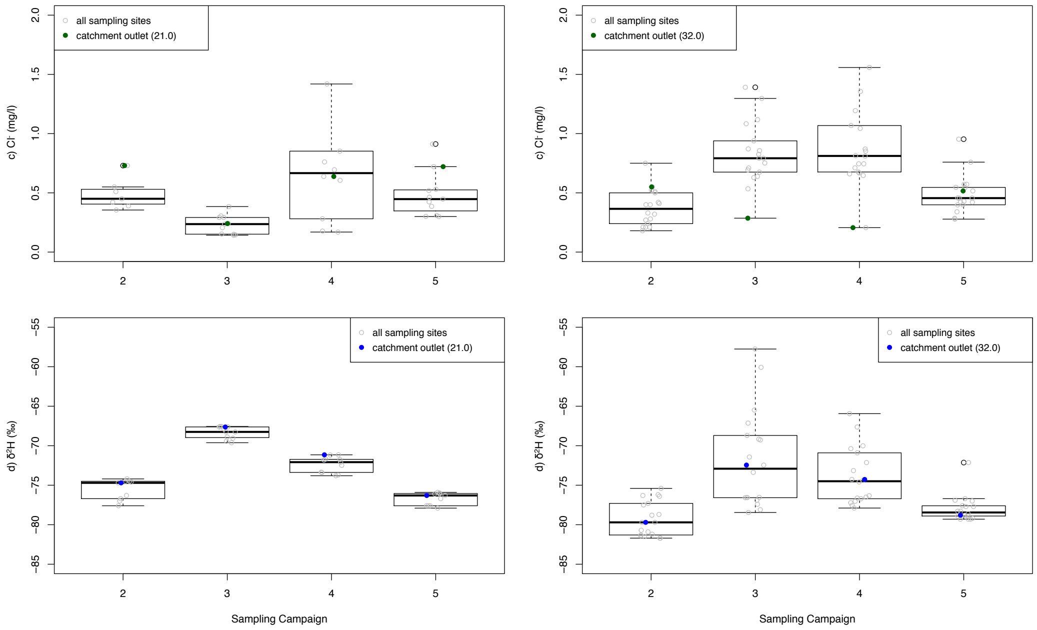


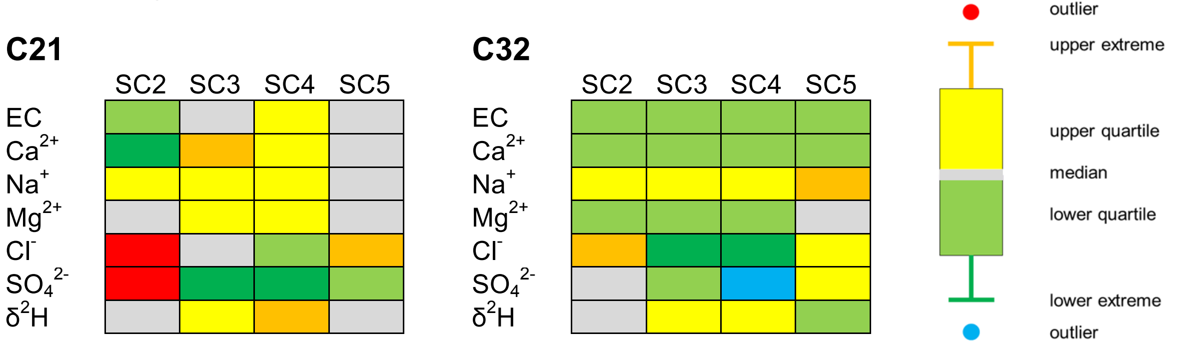
Figure 21f: Boxplots of EC (a), Ca^{2+} (b), Cl^- (c), and δ^2H (d) of all stream sampling sites (grey circles) and the measurement at the outlet (coloured dots) of the catchments (C21: left and C32: right) per SC.

close to that for the measured samples and only in SC4, the outlet was just above the upper quartile (Fig. 21 d, left). In C32 the measured δ^2H was also close to the median value (Fig. 21d, right). Comparison of the measurements of EC, Ca^{2+}, Na^+, Mg^{2+}, Cl^-, SO_4^{2-} and δ^2H at the outlet to the stream samples are summed up in Table 6.

The above results showed many differences in the behavior and spatial distribution of the stream water chemistry for the two catchments. When reducing our observations only to the catchment outlets our main conclusion would be that there were no major differences in the solute concentration between the two catchments but that the solute concentrations were slightly higher in C21 than in C32. Our spatial measurements show that this is not the case and that the concentrations are generally slightly higher in C32 than in C21, and that the concentrations change significantly along the stream reach, indicating the contribution of both high and low ion concentration water to the stream.

Catchment 21

Table 6: Measurement (EC, Ca2+, Na+, Mg2+, Cl-, So42-, 2H) at the outlet compared to samples from the stream in C21 (left) and C32 (right) for all SC.



C21

	SC2	SC3	SC4	SC5
EC	🟩	⬜	🟨	⬜
Ca^{2+}	■	🟧	🟨	⬜
Na^+	🟨	🟨	🟨	⬜
Mg^{2+}	⬜	🟨	🟨	⬜
Cl^-	🟥	⬜	🟩	🟧
SO_4^{2-}	🟥	■	■	🟩
δ^2H	⬜	🟨	🟧	⬜

C32

	SC2	SC3	SC4	SC5
EC	🟩	🟩	🟩	🟩
Ca^{2+}	🟩	🟩	🟩	🟩
Na^+	🟨	🟨	🟨	🟧
Mg^{2+}	🟩	🟩	🟩	⬜
Cl^-	🟧	■	■	🟨
SO_4^{2-}	⬜	🟩	🟦	🟨
δ^2H	⬜	🟨	🟨	🟩

- 🟥 outlier
- 🟧 upper extreme
- 🟨 upper quartile
- ⬜ median
- 🟩 lower quartile
- ■ lower extreme
- 🟦 outlier

5 Discussion and Conclusion

With the four snapshot sampling campaigns, it was possible to show the spatial patterns in stream chemistry along streams and thus, to identify contributing groundwater source areas. Additionally, the two continuous salt tracer measurements corroborated the findings from the snapshot sampling campaigns.

5.1 Spatial and temporal variability in stream chemistry

High spatial variability in streamwater chemistry was observed in similar patterns in all SC. Likens and Buso (2006) observed large variations in streamwater chemistry throughout their whole catchment and Zimmer et al. (2013) found higher chemical variability in their samples from the upstream source areas (groundwater and streamwater) than in their downstream catchment areas. In this study, variability in streamwater chemistry was also observed to be higher in the upper catchment (C32) than in the downstream catchment (C21), whereas variability in the sampled groundwater sources was high in both catchments.

Groundwater and streamwater chemistry (EC, Ca^{2+} and Na^{+}) was generally more comparable in C32 than in C21. This might be an indication that at least in C21, also other groundwater sources, than the sampled areas could contribute to streamwater, e.g. groundwater from deeper source areas that would cause the concentrations to increase between sampling locations 21.25 and 21.21.

Temporal variability was measured in all solutes in both catchments but a clear temporal pattern with higher solute concentrations in the summer (SC3 and SC4) was only observed for EC (GW and Q in C21 and C32), Ca^{2+} concentrations (Q in C21 and GW and Q in C32) and also for the isotopic composition (δ^2H (GW and Q in C21 and C32)). The other solutes did not vary significantly throughout the season (Fig. 8 and Fig. 9 in chapter 4.1 for streamwater and Table 12 for groundwater in the appendix).

5.2 Inferred groundwater source areas

The spatial patterns in stream chemistry along the stream branches during the snapshot sampling campaigns were similar changes for all SC, but the measured concentrations varied for the different campaigns.

In C21, the overall spatial variability in the chemistry of the stream water was small with no sudden changes. Nevertheless, changes in streamwater chemistry along the stream branches were observed and suggest that groundwater contributes to the stream along its branches, but not in greater amounts at specific sites. In the upper parts, groundwater with high ion concentrations contributes to the stream, leading to continuously increasing colute concentration along the stream branch, whereas in the lower part of the stream, groundwater that dilutes the stream water chemistry contributes to the stream flow (Fig 22, left). This might indicate, that in the upper part, groundwater from a deeper source area (e.g. enriched in solutes from bedrock contact) exfiltrates and contributes to the stream. In the lower part, different, small groundwater source areas may contribute to the streamflow. The catchment is characterized by many changes in slopes and steps in topography and is therefore likely to have many springs and areas, where also deep groundwater resurfaces. Streamwater in C21 normally showed lower variability (EC, Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-} and δ^2H) in the different SC, than the groundwater from the surrounding wells, which is also an indicator for many different groundwater source areas contributing to streamflow.

As no major inflows were detected from the spatial analysis of chemical and isotopic variations in the streamwater in C21, the aim of the salt tracer experiment was, to find such (major) groundwater contributions to the stream and to quantify it. The location of the start of the experiment was determined by a stream section, where the stream reconnects,

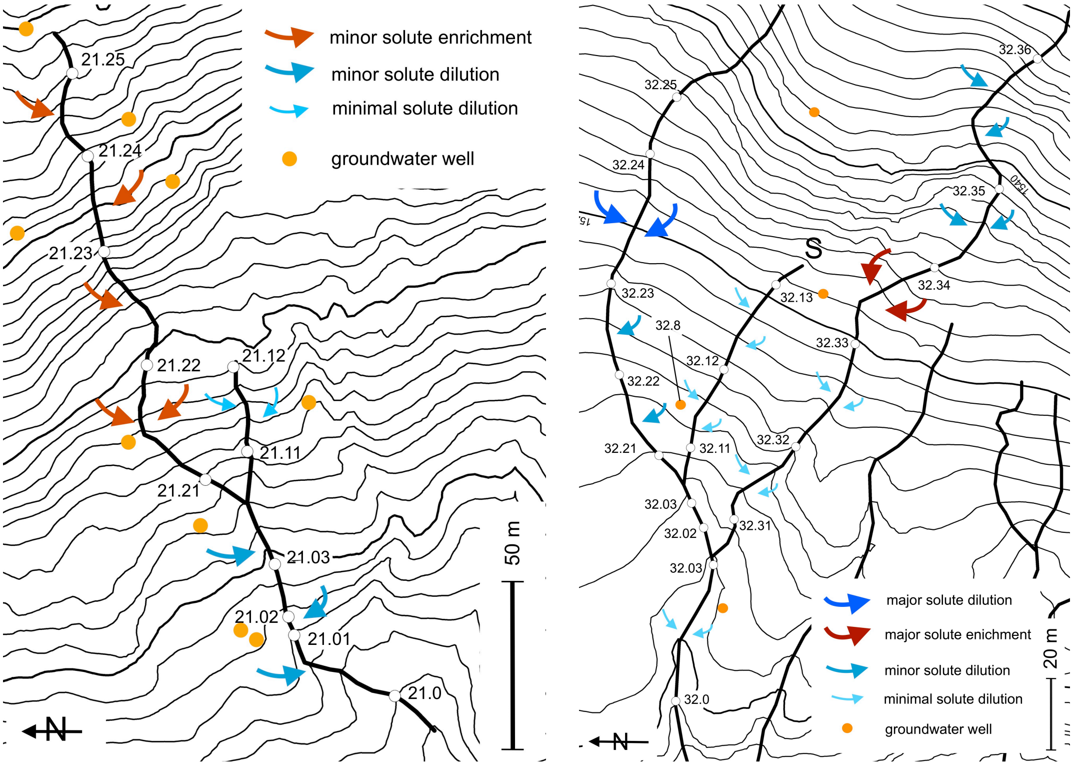


Figure 22: Maps oft he infered groundwater contributions to streamflow in C21 (left) and C32 (right).

after it divided into several smaller streams. Because a steady state (constant EC at catchment outlet) had to be reached, it was decided to focus on a shorter stream section to ensure results for at least this section. Generally, in the steeper, first section (10 – 30 m) the EC decreased more than in the flatter stream sections (40 – 125 m). Sudden decreases in EC were only measured at the confluences with the other branch (branch 1) and the side contribution from a wet area some 35 meters downstream from the confluence. This suggests that groundwater contributed to the stream in the steep part, while there was very little contribution from groundwater to streamwater in the flatter part of the stream. Comparing these findings to the interpretation from the changes in streamwater chemistry, the changes along the lower stream sections might be more related to the mixing of the 2 branches than to the contributions from groundwater.

In C32, small changes in streamwater chemistry along the branches and major, sudden changes in stream chemistry were observed for all sampling campaigns. These findings indicate, that diffuse groundwater exfiltration contributes to the stream in smaller amounts and that at specific spots, there is a much larger groundwater contribution to the stream.

These major contribution sites in C32 (Fig. 22, right) had a distinctly different effect on the streamwater chemistry: while in stream branch 3, between sampling sites 32.34 and 32.33, it generally increased the EC and the solute concentrations of the stream, in stream branch 2, between sites 32.24 and 32.23, it caused a significant drop in EC and also in the solute concentration. δ^2H became less depleted in between the sampling locations 32.24 and 32.23 in SC3 and SC4, for which the recent rain also had a distinctly less depleted signature (-16 and -41 ‰ before SC3 and SC4 compared to -98 ‰ before SC5). Between the sampling sites 32.34 and 32.33 in stream branch 3, δ2H became less depleted downstream of the major contribution in SC3, while in the other sampling campaigns, stream water δ2H became more depleted after the major contribution. These different effects on the streamwater chemistry indicate that different groundwater sources contribute to the different stream sections. As both discussed zones are located at a change in slope (from steep to gentle), and they are at the same elevation as the spring (Fig. 22, right: S), supplying water to branch 1, it is assumed that the major contributions to the stream could come from deeper groundwater areas or maybe from a specific layer in the Flysch with high flow. While in branch 3, the major contribution shows the signature of deep groundwater (higher solute concentrations), in branch 2, another groundwater source (with extremely low solute concentration) is contributing to stream flow. It has to be mentioned that close by the major contribution site to branch 2, the groundwater well 32.8 was sampled, which had a very low EC (110 and 194 µS/cm) in SC2 and SC3, when also the solute concentrations were low. Though, in the other SC, EC and chemical composition was more comparable to the other samples of shallow groundwater within the catchment. This could suggest, that the shallow groundwater, measured from the well 32.8, is in contact to the other groundwater source, showing the extremely low solute concentrations. Continuous contributions along the stream could not be linked directly to one of the sampled groundwater sources. Rather it is assumed, that several shallow groundwater source areas are connected and together contribute to the streamflow.

In C32, the aim was to investigate the major inflows (on branch 2 and 3) detected in the spatial analysis of chemical and isotopic composition but due to insufficient stream flow, the experiment in branch 2 was not possible and the experiment at branch 3 was only possible when we started right below the interesting inflow spot on branch 3. However, the fact that there was only little flow upstream from the major inflow spot and that there was enough flow below this site, is an indication for a major groundwater contribution to streamflow in this area. Yet, it was possible to find a stream section of ~ 125 m, where the experiment could be carried out (see Fig. 6; Chapter 3.2.2). The largest decrease in measured EC (most inflow from groundwater to stream) was measured in the first ~ 65 m from the start of the experiment, which corresponds to the findings from the snapshot sampling campaigns, where also decreasing solute concentrations were observed in this steep stream section. These first 65 m were located in steeper terrain, while no major dilution of EC was measured in the gentle slope sections of the stream. A major, sudden decrease in EC was only measured at the confluence with the other branches. This corresponds to the experiments results from C21; groundwater was contributing to the stream in the steep stream section, while there was only very little contribution from the groundwater to the streamwater in the flatter parts of the stream. Major, sudden groundwater contributions to the stream were not detected from the experiment.

In both catchments, an estimation of groundwater contribution to the stream in the steep parts (25 ml/s/m in branch 2, C21 compared to 1 ml/s/m in branch 3, C32) was made from the continuous salt tracer measurements. The two investigated streams also showed a different stream discharge before the area, where groundwater contribution to the stream was measured (300 ml/s in C21 and 200 ml/s in C32) but this does not explain the large difference. For the estimation, the mean EC of the closest groundwater well was taken, which might not be very representative for the groundwater contribution to the stream because of the high variability between the measured groundwater sources. Nevertheless, the higher contribution from groundwater to the stream in C21 was also observed while the experiment was performed because the runoff was significantly higher after the investigated stream section in C21.

Fischer et al. (2015) found a less depleted δ^2H signature in his October 2011 sampling campaign than in his June 2011 sampling campaign in the whole Zwäckentobel catchment. In this master's thesis, the stream- and groundwater also had less depleted δ2H for the SC3 to SC5 from August to October 2016 than for the SC2 in July, 2016. Furthermore, Fischer et al. (2015) show that Ca^{2+} concentrations decrease from the spring zone of the Studibach catchment (which would be C32 for this study) towards the catchment outlet (which would be below C21). Such a decrease in solute concentration from the upper to the lower catchment (dilution) was also observed pronounced in the groundwater and less pronounced in the streamwater in this master's thesis. Singh et al. (2016) observed that stream water became enriched in δ18O from the heads towards the outlet of the catchment. In this study, δ^2H was also less depleted in the lower catchment (C21) than in the upper catchment (C32).

5.3 Topography and land use

As mentioned in chapter 4.3, there were large differences in the chemical composition and the groundwater inflows between steep and gentle slope sampling sites. Furthermore, significant differences were found between the two catchments. In C21, samples from steep sampling sites had generally lower EC and Ca^{2+} concentrations, while in C32, the samples from the steep sampling locations had higher EC and higher Ca^{2+} concentrations (Fig. 15, Chapter 4.3.1). An exception is the sampling location 21.12 in C21. This location is in steep terrain but had (in contrast to all other steep locations in C21) high EC and Ca^{2+} concentrations in all SC. Similar differences were also found in Na^{+} and Mg^{2+} as well as in δ^2H. This opposite pattern for the two catchments can't be fully explained without further research.

In both catchments, there was more groundwater flowing into the stream in steep stream sections, which means that the here observed opposite pattern has to be explained by different groundwater contributing to the stream flow. The median observed groundwater EC and Ca^{2+}- and Na^{+} concentrations were significantly higher in C21 than in C32 (Fig. 12). In both catchments, high variability was observed between the different groundwater sources. In C32, the major contribution in stream branch 3, between sampling locations 32.33 and 32.34 showed the signal of deep groundwater, enriching the streamflow with solutes (Fig. 22, right). C21 is characterized by many changes in slope and steps in topography. As mentioned in the introduction, groundwater is likely to resurface at such steps or changes in slope. Therefore, it might be possible that in catchment 21, the groundwater contributing to the upper stream section, enriching the solute concentration of the stream section continuously (21.25 to 21.21; Fig. 22, left) comes from deeper groundwater sources (Fig. 23). The mentioned lower similarity between groundwater and streamwater in C21 (chapter 4.1 and 5.1) supports this theory. Also noticeable is that the geology of C21 is Waegitaler Flysch, while for C32 it is mostly Schlieren Flysch. Geology was not further investigated in this thesis but might be an interesting factor for future research in this area.

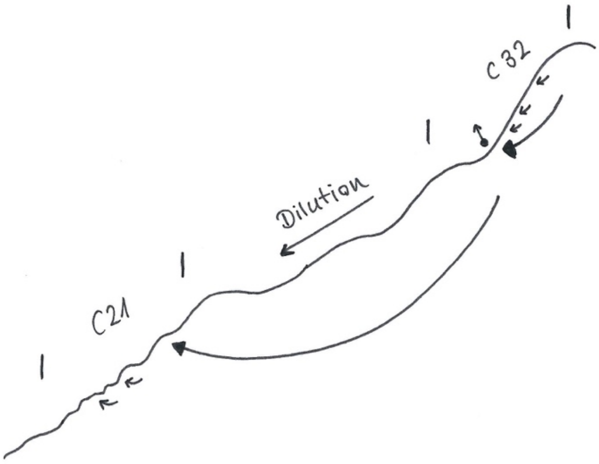


Figure 23: draft of the groundwater contribution to the stream in both investigated catchments.

Chemical and isotopic changes along the stream could not clearly be linked to land use changes in either catchment. In C32 this might have two major reasons: first, the investigated stream sections were generally short and therefore not flowing through many different land use areas. Secondly, the stream was surrounded by meadows, except for the last 50 meters of the stream before the outlet, where on the left side when looking downstream (i.e. south side), there was a wetland. Again due to the short distance, the small spatial variations in hydrochemistry and the fact, that three branches come together right upstream of this section and mix, it is not possible to make a statement about the role of this wetland area.

In C21, the stream is flowing through different land uses, but the observed changes were not directly related to land use and continued even if the stream flowed through another land use. Only between sampling locations 21.22 and 21.21, where the stream flows from a moor into the forest, pronounced changes in stream water EC and δ^2H were found to correlate with the change in land use. Without further research, it is not possible to make a conclusion whether this change in solute concentration comes from the observed groundwater contribution to the stream or also from the change in land use.

5.4 Representativeness of the catchment outlet for the catchment

No general statement on the representativeness of the catchment outlets can be made. For some components, such as EC, δ^2H, Ca^{2+}, Na^+ and Mg^{2+}, the sample at the catchment outlet was generally close to the median of the samples along the stream but for Cl^- and SO_4^{2-} concentrations, the measurements at the outlet were an extreme value or even an outlier in several SC.

If only measurements at the outlet of the catchments were taken, an antithetical temporal variability for a catchment would have been observed: e.g. in C32, lower Cl^- concentrations were measured at the catchment outlet for SC3 and SC4 than for the other SCs, but when all samples from the stream are considered, Ca^{2+} concentrations were actually higher for SC3 and SC4 and lower for SC2 and SC5 (Fig. 21c, right).

Especially in C32, the large variability within the catchment would not have been known based on samples from only the outlet samples. The two interesting sites in C32, where solute concentration suddenly increased or started to gradually decrease significantly also not have been found.

Considering the measured spatial variability within the two catchment, both outlets are located at a representative spot. They are both located after the confluence of difference stream branches, so the streamwater has had enough time to mix before the sample is taken.

5.5 Conclusion and further research topics

Spatial and temporal variability in stream water chemistry and isotopic composition as well as contributing groundwater source areas were observed from the performed snapshot sampling campaigns. While there was a similar pattern for the spatial variability in solute concentration of streamwater in all SCs, temporal changes in streamwater chemistry were observed too, but no clear pattern could be observed. Furthermore, significant differences in streamwater chemistry were found within and between the two catchments. With the continuous salt tracer measurements in the two catchments, some of the identified potential groundwater contribution areas could be verified and quantified. The spatial variability in streamwater was linked to contribution from different groundwater source areas. A clear statement about the representativeness of a measurement at the catchment outlet can’t be formulated. Measuring the outlet of a catchment may or may not give an average mean solute concentration of the catchment and intra-catchment variability will never be detected by the outlet measurement.

Fischer et al. 2015 mentions, that a main reason why headwaters and small streams are largely unstudied is the accessibility of these areas. In this study, snapshot sampling proved not only to be useful to locate groundwater contributions to the stream, but was also easy to perform. The equipment needed for measurements (WTW, probe, fieldbook) and sampling (plastic bottles, syringe) is neither much, nor heavy to carry in a backpack. Consequently, in my opinion, the difficult accessibility of an area should be no reason why a catchment is not investigated. Snapshot sampling campaigns are feasible in all areas that are accessible by hiking. Further studies on groundwater – streamwater interactions in headwater catchments and small streams are needed because of the dominance and great importance of these small streams (Wohl, 2017; Downing et al. 2012).

The conducted continuous salt tracer experiments in this study provided interesting results on subsurface inflow to the streams and verified and quantified the groundwater contributions, observed from the snapshot sampling campaigns. The equipment needed to perform the experiment is neither expensive nor hard to find. A simple but nevertheless functioning mariotte bottle can be self-made from a plastic canister, some tubes and sealing material. To create a functioning mariotte bottle, air is not allowed any other way into the bottle than through the tube at the top. If this is not guaranteed, the injection rate will not be stable and the experiment will not work. The salt can be bought in every store and the water to mix the brine can normally be found within the catchment. However, the water should be taken from a different stream branch in order not to disturb the stream branch under investigation. For continuous salt tracer measurements I would suggest (also or especially in small streams), to use two mariotte bottles in order to avoid interruptions in the injection rate of the brine, when one bottle gets empty and has to be refilled. To reach a steady state (constant EC at the end of the streams experiment section) is essential in order to perform the measurements of the experiment. Therefore, it is vital to not have any gaps in the brine injection. In catchment 21, the experiment stream section was limited by an upslope area, where the stream separated into several smaller streams before the main stream branch was reformed again. With more time, it would be interesting to test, if such a section really has to be a limiting factor or if the experiment could still be conducted. In several stream segments in C32, small ponds were observed, where the water probably stayed for a longer time. Also there it would be interesting to know if such ponds reduce the feasibility of continuous salt tracer experiments.

If I only were to use one of the described methods, I would still focus on the snapshot sampling because many different chemical components can be measured along several branches at the same time and potential groundwater contribution areas could be identified as well. Also if the focus of a study lies on the groundwater contribution sites, I would suggest to first perform a snapshot sampling campaign or at least some EC measurement series along the streams in order to find potential groundwater source areas. The continuous salt tracer measurements need a lot of time and it is therefore useful to know which sections are likely to show subsurface groundwater contribution to the streamflow.

In the Alptal catchments, many studies were (Rinderer et al. 2014, 2016; Fischer et al. 2015) and still are conducted (PhD Project, Leonie Kiewiet) on shallow groundwater and a lot of knowledge has been generated. In this research, locations where groundwater contributes to the streams were determined. It would be interesting to see, where this groundwater comes from. This could be done by artificial tracers like fluorescent dye or salt (Leibundgut and Seibert, 2011). The visible tracers could be injected into the groundwater through the groundwater wells and then the inflow (where and when) to the streams could be observed or measured with a fluorometer or EC meter.

This thesis, suggests, that deep groundwater could be a contributing source to streamwater. It would be interesting to investigate the age of this water (for example through age dating with CFCs or Tritium) and to see if there are deep groundwater sources contributing to the Zwäckentobel area as well.

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Appendix A: Tables

Table 7: Kruskal-Wallis significance test of EC, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and δ^2H in groundwater compared to streamwater per catcment and sampling campaign.

EC	C 21 (GW vs. Q)		C 32 (GW vs. Q)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.0013	Significant	0.4561	Non-Significant
SC 3	0.0002	Significant	0.7897	Non-Significant
SC 4	0.0002	Significant	0.0277	Significant
SC 5	0.0002	Significant	0.4836	Non-Significant

Ca^{2+}	C 21 (GW vs. Q)		C 32 (GW vs. Q)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.0021	Significant	0.4561	Non-Significant
SC 3	0.0002	Significant	0.7389	Non-Significant
SC 4	0.0005	Significant	0.9468	Non-Significant
SC 5	0.0007	Significant	0.9468	Non-Significant

Mg^{2+}	C 21 (GW vs. Q)		C 32 (GW vs. Q)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.9233	Non-Significant	0.0008	Significant
SC 3	0.1599	Non-Significant	0.0278	Significant
SC 4	0.5184	Non-Significant	0.0329	Significant
SC 5	0.1837	Non-Significant	0.0196	Significant

Na^{+}	C 21 (GW vs. Q)		C 32 (GW vs. Q)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.1019	Non-Significant	0.0736	Non-Significant
SC 3	0.0167	Significant	0.1615	Non-Significant
SC 4	0.0304	Significant	0.0196	Significant
SC 5	0.0070	Significant	0.0136	Significant

Cl^{-}	C 21 (GW vs. Q)		C 32 (GW vs. Q)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.4428	Non-Significant	0.0308	Significant
SC 3	0.8493	Non-Significant	0.2569	Non-Significant
SC 4	0.5136	Non-Significant	0.7165	Non-Significant
SC 5	0.0019	Significant	0.0009	Significant

SO_4^{2-}	C 21 (GW vs. Q)		C 32 (GW vs. Q)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.9062	Non-Significant	0.0208	Significant
SC 3	0.5184	Non-Significant	0.0830	Non-Significant
SC 4	0.2885	Non-Significant	0.0251	Significant
SC 5	0.2205	Non-Significant	0.0830	Non-Significant

δ^2H	C 21 (GW vs. Q)		C 32 (GW vs. Q)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.1022	Non-Significant	0.0022	Significant
SC 3	0.2098	Non-Significant	0.0388	Significant
SC 4	0.5688	Non-Significant	0.0196	Significant
SC 5	0.1097	Non-Significant	0.1350	Non-Significant

Table 8: Mean and SD of EC, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and δ^2H in groundwater compared to streamwater per catchment and sampling campaign.

EC	C 21 - GW			C21 - Q			C 32 - GW			C32 - Q		
(µS/cm)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	9	417	74.1	9	290	9.3	5	300	110.5	18	312	33.5
SC 3	9	477	72.7	11	331	15.0	6	326	66.7	18	326	43.4
SC 4	9	510	88.8	11	335	22.1	6	391	54.3	18	312	63.2
SC 5	9	501	69.3	11	316	18.0	6	356	64.0	18	314	55.3

Ca^{2+}	C 21 - GW			C21 - Q			C 32 - GW			C32 - Q		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	9	45.1	7.8	9	33.7	0.9	5	33.9	12.6	18	35.5	3.7
SC 3	9	91.6	13.2	11	58.1	2.7	6	55.1	14.9	18	54.9	8.2
SC 4	9	82.4	14.1	11	59.6	3.8	6	53.4	13.9	18	54.0	11.1
SC 5	9	84.2	12.6	11	53.9	2.1	6	52.5	10.0	18	52.5	9.6

Mg^{2+}	C 21 - GW			C21 - Q			C 32 - GW			C32 - Q		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	9	2.0	1.0	9	1.6	0.3	5	0.6	0.2	18	1.8	0.4
SC 3	9	3.3	1.7	11	2.2	0.4	6	1.5	1.4	18	2.3	0.6
SC 4	9	2.8	1.3	11	2.2	0.5	6	1.4	1.4	18	2.0	0.6
SC 5	9	3.3	1.2	11	2.4	0.5	6	1.5	1.4	18	2.4	0.6

Na^{+}	C 21 - GW			C21 - Q			C 32 - GW			C32 - Q		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	9	0.8	0.5	9	1.0	0.4	5	0.6	0.3	18	0.9	0.2
SC 3	9	1.3	1.0	11	1.8	0.5	6	0.9	0.4	18	1.2	0.4
SC 4	9	1.1	0.8	11	1.9	0.8	6	0.6	0.3	18	1.1	0.3
SC 5	9	1.0	0.8	11	2.0	0.8	6	0.6	0.4	18	1.2	0.4

Cl^{-}	C 21 - GW			C21 - Q			C 32 - GW			C32 - Q		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	9	0.7	0.3	7	0.5	0.1	5	0.9	0.6	18	0.4	0.1
SC 3	9	0.3	0.2	11	0.2	0.1	6	0.9	0.1	18	0.8	0.3
SC 4	9	1.2	1.0	11	1.1	1.5	7	1.0	0.3	18	1.1	1.1
SC 5	9	0.9	0.2	11	0.5	0.2	6	1.2	0.4	18	0.5	0.2

SO_4^{2-}	C 21 - GW			C21 - Q			C 32 - GW			C32 - Q		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	9	4.0	3.8	7	3.1	0.5	5	2.1	1.1	18	5.9	3.5
SC 3	9	4.5	6.1	11	2.7	0.5	6	4.3	2.2	18	7.1	2.8
SC 4	9	6.9	8.3	11	5.6	3.5	7	4.5	2.7	18	8.1	3.6
SC 5	9	8.6	11.6	11	5.1	1.1	6	4.4	2.4	18	6.6	2.7

δ^2H	C 21 - GW			C21 - Q			C 32 - GW			C32 - Q		
(‰)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	9	-78.5	3.8	9	-75.6	1.2	4	-71.9	1.9	18	-79.2	2.2
SC 3	9	-73.4	6.7	11	-68.3	0.7	6	-61.4	9.3	18	-71.8	6.0
SC 4	9	-73.6	4.3	11	-72.4	1.0	8	-68.8	5.0	18	-73.8	3.5
SC 5	9	-75.7	3.1	11	-76.7	0.8	5	-76.4	2.4	18	-78.0	1.6

Table 9: Kruskal-Wallis significance test of EC, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and δ^2H in steep vs. gentle slopes per catchment and sampling campaign.

EC	C 21 (steep vs. genlte slopes)		C 32 (steep vs. genlte slopes)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.2187	Non-Significant	0.0469	Significant
SC 3	0.1003	Non-Significant	0.0017	Significant
SC 4	0.1003	Non-Significant	0.0013	Significant
SC 5	0.0996	Non-Significant	0.0071	Significant

Ca^{2+}	C 21 (steep vs. genlte slopes)		C 32 (steep vs. genlte slopes)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.4624	Non-Significant	0.0380	Significant
SC 3	0.0679	Non-Significant	0.0023	Significant
SC 4	0.1003	Non-Significant	0.0013	Significant
SC 5	0.1003	Non-Significant	0.0071	Significant

Mg^{2+}	C 21 (steep vs. genlte slopes)		C 32 (steep vs. genlte slopes)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.3272	Non-Significant	0.3538	Non-Significant
SC 3	0.1003	Non-Significant	0.0576	Non-Significant
SC 4	0.1441	Non-Significant	0.0703	Non-Significant
SC 5	0.3613	Non-Significant	0.1023	Non-Significant

Na^{+}	C 21 (steep vs. genlte slopes)		C 32 (steep vs. genlte slopes)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.6242	Non-Significant	0.3538	Non-Significant
SC 3	0.1441	Non-Significant	0.2004	Non-Significant
SC 4	0.3613	Non-Significant	0.3538	Non-Significant
SC 5	0.3613	Non-Significant	0.6911	Non-Significant

Cl^{-}	C 21 (steep vs. genlte slopes)		C 32 (steep vs. genlte slopes)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.3613	Non-Significant	0.0630	Non-Significant
SC 3	0.5219	Non-Significant	1.0000	Non-Significant
SC 4	0.2008	Non-Significant	0.4797	Non-Significant
SC 5	0.8551	Non-Significant	0.8946	Non-Significant

SO_4^{2-}	C 21 (steep vs. genlte slopes)		C 32 (steep vs. genlte slopes)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.6985	Non-Significant	0.1711	Non-Significant
SC 3	0.0446	Significant	0.3311	Non-Significant
SC 4	0.3938	Non-Significant	0.2697	Non-Significant
SC 5	0.8548	Non-Significant	0.2697	Non-Significant

δ^2H	C 21 (steep vs. genlte slopes)		C 32 (steep vs. genlte slopes)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
SC 2	0.1400	Non-Significant	0.3309	Non-Significant
SC 3	0.0104	Significant	0.0023	Significant
SC 4	0.0062	Significant	0.0243	Significant
SC 5	0.0519	Non-Significant	0.9293	Non-Significant

Table 10: Mean and SD of EC, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and δ^2H in steep compared to gentle slopes per catchment and sampling campaign.

EC	C 21 - gentle slopes			C21 - steep slopes			C 32 - gentle slopes			C32 - steep slopes		
(μS/cm)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	4	295	7.1	5	286	9.2	9	295	35.2	9	328	21.3
SC 3	6	338	6.7	5	321	16.7	9	297	42.2	9	355	17.3
SC 4	6	345	13.4	5	323	24.2	9	266	58.4	9	358	16.0
SC 5	6	323	12.8	5	308	19.7	9	278	54.6	9	349	25.0

Ca^{2+}	C 21 - gentle slopes			C21 - steep slopes			C 32 - gentle slopes			C32 - steep slopes		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	4	34.0	1.0	5	33.4	0.7	9	33.7	3.8	9	37.4	2.4
SC 3	6	59.5	1.5	5	56.3	2.7	9	49.4	8.0	9	60.4	3.4
SC 4	6	61.9	1.6	5	56.8	3.9	9	45.8	10.3	9	62.2	2.9
SC 5	6	54.8	1.7	5	52.9	2.2	9	46.2	9.3	9	58.9	4.3

Mg^{2+}	C 21 - gentle slopes			C21 - steep slopes			C 32 - gentle slopes			C32 - steep slopes		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	4	1.7	0.3	5	1.6	0.3	9	1.7	0.4	9	1.9	0.3
SC 3	6	2.3	0.3	5	2.1	0.4	9	2.0	0.6	9	2.6	0.3
SC 4	6	2.4	0.4	5	2.0	0.5	9	1.7	0.6	9	2.3	0.3
SC 5	6	2.5	0.4	5	2.2	0.5	9	2.2	0.6	9	2.7	0.4

Na^{+} (mg/l)	C 21 - Q(gentle slopes)			C21 - Q(steep slopes)			C 32 - Q(gentle slopes)			C32 - Q(steep slopes)		
	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	4	1.1	0.4	5	0.9	0.4	9	0.9	0.2	9	0.9	0.1
SC 3	6	1.9	0.4	5	1.7	0.5	9	1.1	0.5	9	1.3	0.3
SC 4	6	2.2	0.7	5	1.5	0.8	9	1.0	0.4	9	1.2	0.2
SC 5	6	2.2	0.7	5	1.7	0.8	9	1.2	0.4	9	1.3	0.3

Cl^{-}	C 21 - gentle slopes			C21 - steep slopes			C 32 - gentle slopes			C32 - steep slopes		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	2	0.6	0.2	5	0.5	0.1	9	0.4	0.1	9	0.3	0.2
SC 3	6	0.2	0.1	5	0.2	0.1	9	0.8	0.3	9	0.8	0.2
SC 4	6	1.3	1.9	5	0.9	0.3	9	0.8	0.4	9	1.4	1.5
SC 5	6	0.5	0.1	5	0.5	0.2	9	0.5	0.1	9	0.5	0.2

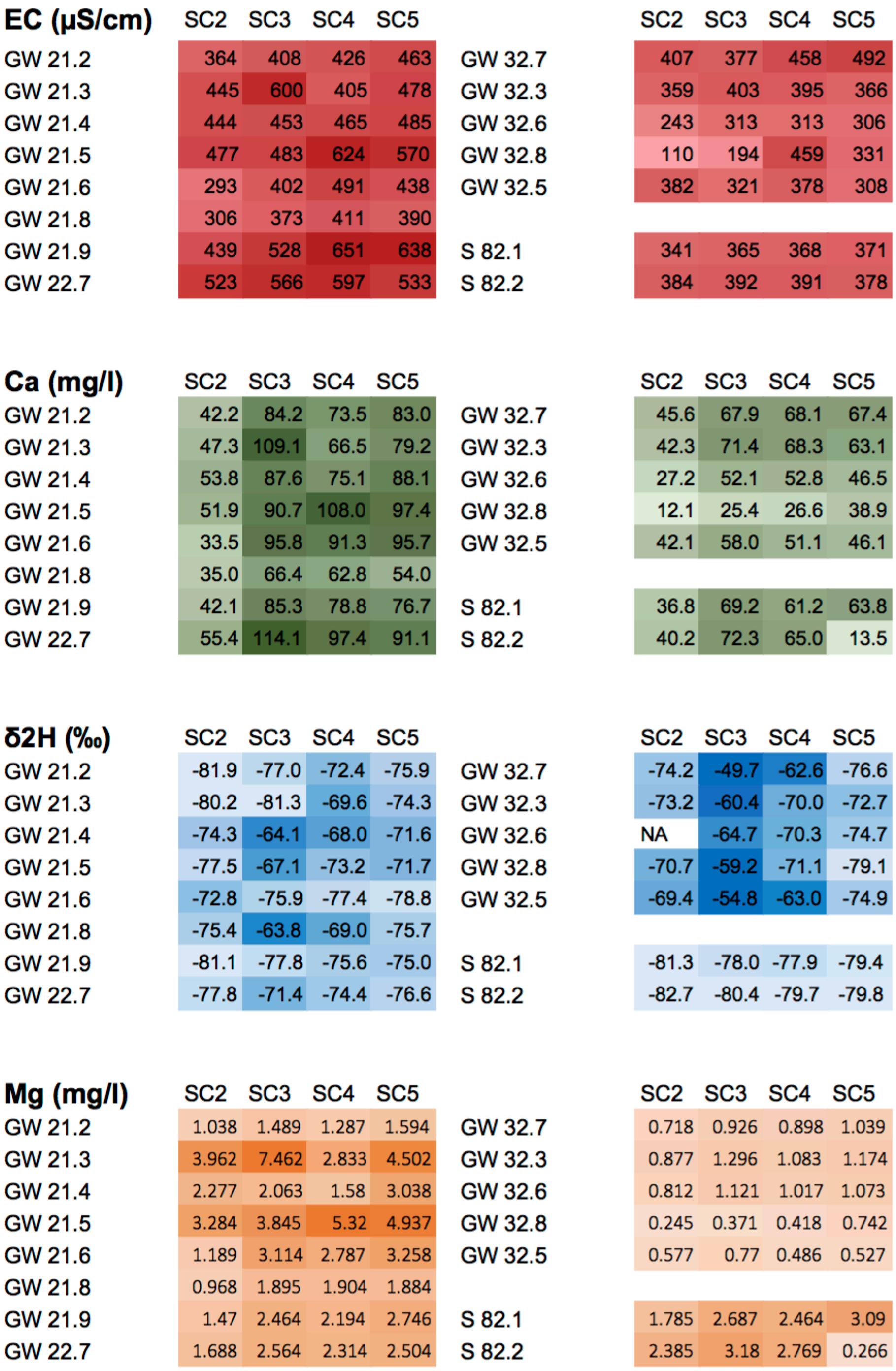
SO_4^{2-}	C 21 - gentle slopes			C21 - steep slopes			C 32 - gentle slopes			C32 - steep slopes		
(mg/l)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	2	3.5	0.7	5	3.0	0.2	9	4.6	1.7	9	7.2	4.2
SC 3	6	2.4	0.5	5	3.1	0.2	9	6.4	3.0	9	7.8	2.3
SC 4	6	5.6	4.5	5	5.7	0.7	9	7.2	3.5	9	9.0	3.3
SC 5	6	5.0	1.0	5	5.3	1.2	9	5.8	2.9	9	7.4	2.2

δ^2H	C 21 - gentle slopes			C21 - steep slopes			C 32 - gentle slopes			C32 - steep slopes		
(‰)	n	mean	SD	n	mean	SD	n	mean	SD	n	mean	SD
SC 2	4	-74.6	0.1	5	-76.4	1.1	9	-78.8	2.0	9	-79.7	2.2
SC 3	6	-67.8	0.3	5	-69.1	0.5	9	-67.5	5.1	9	-76.0	3.2
SC 4	6	-71.6	0.3	5	-73.4	0.5	9	-71.9	3.7	9	-75.8	1.9
SC 5	6	-76.2	0.3	5	-77.3	0.7	9	-78.4	0.5	9	-77.6	2.2

Table 11: Kruskal-Wallis significance test of EC, Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and δ^2H in steep vs. gentle slopes per catchment over all sampling campaigns

	C 21 (steep vs. gentle slopes)		C 32 (steep vs. gentle slopes)	
	p-value	Significance - test (alpha = 0.05)	p-value	Significance - test (alpha = 0.05)
EC	0.0126	Significant	1.16E-08	Significant
Ca^{2+}	0.0219	Significant	2.80E-05	Significant
Na^{+}	0.0167	Significant	6.47E-02	Non-Significant
Mg^{2+}	1.46E-02	Significant	1.33E-03	Significant
Cl^{-}	0.3051	Non-Significant	0.8880	Non-Significant
SO_4^{2-}	0.3538	Non-Significant	0.0254	Significant
δ^2H	0.0677	Non-Significant	0.0664	Non-Significant

Table 12: Temporal and spatial variability in groundwater in C21 (felt) and C32 (right) for all SC.



EC (µS/cm)	SC2	SC3	SC4	SC5		SC2	SC3	SC4	SC5
GW 21.2	364	408	426	463	GW 32.7	407	377	458	492
GW 21.3	445	600	405	478	GW 32.3	359	403	395	366
GW 21.4	444	453	465	485	GW 32.6	243	313	313	306
GW 21.5	477	483	624	570	GW 32.8	110	194	459	331
GW 21.6	293	402	491	438	GW 32.5	382	321	378	308
GW 21.8	306	373	411	390					
GW 21.9	439	528	651	638	S 82.1	341	365	368	371
GW 22.7	523	566	597	533	S 82.2	384	392	391	378

Ca (mg/l)	SC2	SC3	SC4	SC5		SC2	SC3	SC4	SC5
GW 21.2	42.2	84.2	73.5	83.0	GW 32.7	45.6	67.9	68.1	67.4
GW 21.3	47.3	109.1	66.5	79.2	GW 32.3	42.3	71.4	68.3	63.1
GW 21.4	53.8	87.6	75.1	88.1	GW 32.6	27.2	52.1	52.8	46.5
GW 21.5	51.9	90.7	108.0	97.4	GW 32.8	12.1	25.4	26.6	38.9
GW 21.6	33.5	95.8	91.3	95.7	GW 32.5	42.1	58.0	51.1	46.1
GW 21.8	35.0	66.4	62.8	54.0					
GW 21.9	42.1	85.3	78.8	76.7	S 82.1	36.8	69.2	61.2	63.8
GW 22.7	55.4	114.1	97.4	91.1	S 82.2	40.2	72.3	65.0	13.5

δ2H (‰)	SC2	SC3	SC4	SC5		SC2	SC3	SC4	SC5
GW 21.2	-81.9	-77.0	-72.4	-75.9	GW 32.7	-74.2	-49.7	-62.6	-76.6
GW 21.3	-80.2	-81.3	-69.6	-74.3	GW 32.3	-73.2	-60.4	-70.0	-72.7
GW 21.4	-74.3	-64.1	-68.0	-71.6	GW 32.6	NA	-64.7	-70.3	-74.7
GW 21.5	-77.5	-67.1	-73.2	-71.7	GW 32.8	-70.7	-59.2	-71.1	-79.1
GW 21.6	-72.8	-75.9	-77.4	-78.8	GW 32.5	-69.4	-54.8	-63.0	-74.9
GW 21.8	-75.4	-63.8	-69.0	-75.7					
GW 21.9	-81.1	-77.8	-75.6	-75.0	S 82.1	-81.3	-78.0	-77.9	-79.4
GW 22.7	-77.8	-71.4	-74.4	-76.6	S 82.2	-82.7	-80.4	-79.7	-79.8

Mg (mg/l)	SC2	SC3	SC4	SC5		SC2	SC3	SC4	SC5
GW 21.2	1.038	1.489	1.287	1.594	GW 32.7	0.718	0.926	0.898	1.039
GW 21.3	3.962	7.462	2.833	4.502	GW 32.3	0.877	1.296	1.083	1.174
GW 21.4	2.277	2.063	1.58	3.038	GW 32.6	0.812	1.121	1.017	1.073
GW 21.5	3.284	3.845	5.32	4.937	GW 32.8	0.245	0.371	0.418	0.742
GW 21.6	1.189	3.114	2.787	3.258	GW 32.5	0.577	0.77	0.486	0.527
GW 21.8	0.968	1.895	1.904	1.884					
GW 21.9	1.47	2.464	2.194	2.746	S 82.1	1.785	2.687	2.464	3.09
GW 22.7	1.688	2.564	2.314	2.504	S 82.2	2.385	3.18	2.769	0.266

Appendix B: Figures

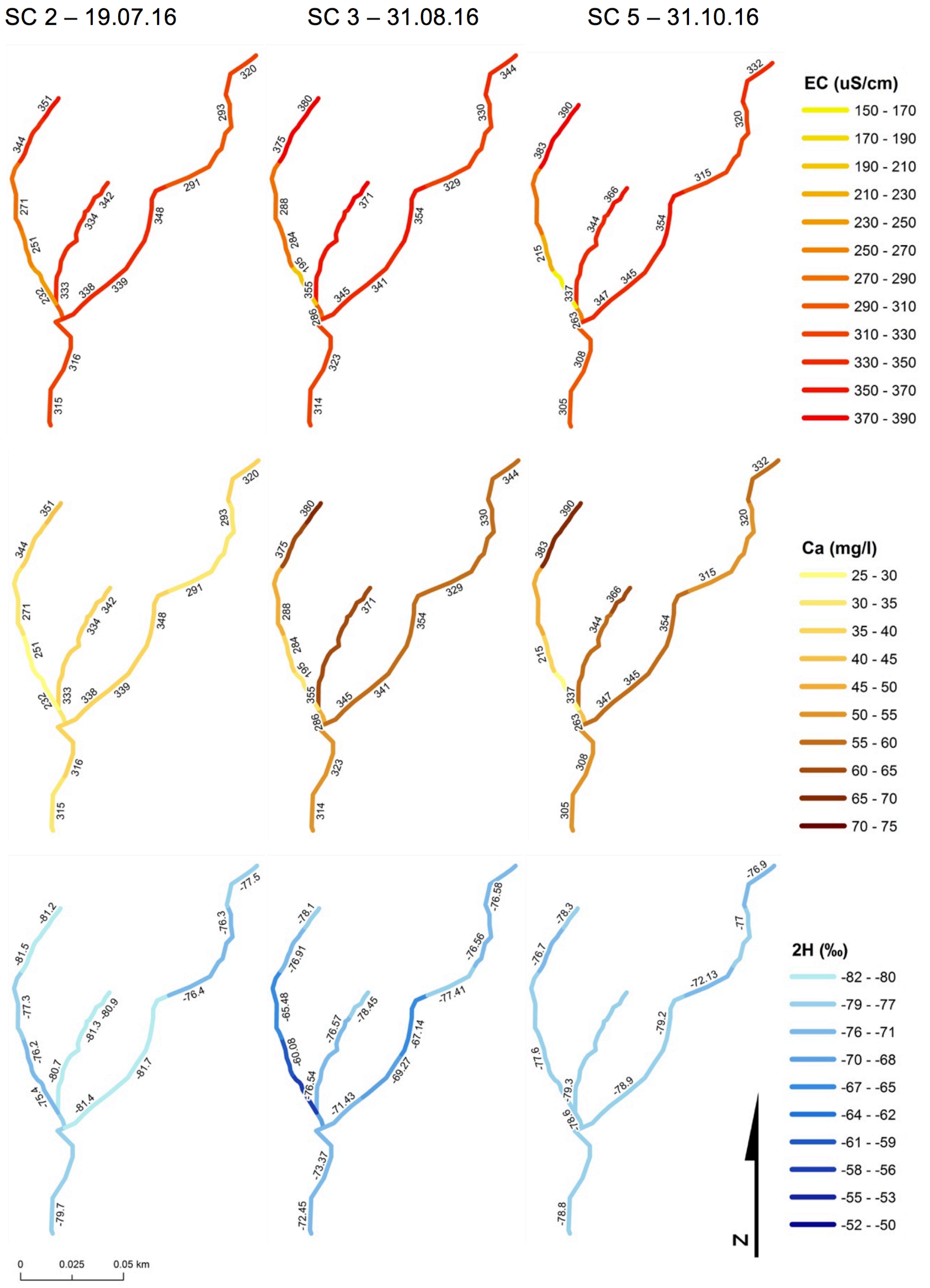


Figure 24: Maps of EC, Ca^{2+} concentration and δ^2H (top to bottom) along stream branches in **C32** measured in SC2, SC3 and SC5 (left to right). The maps of SC 4 are displayed in the results section (Chapter 4). The maps of SC 4 are displayed in the results section (Chapter 4).

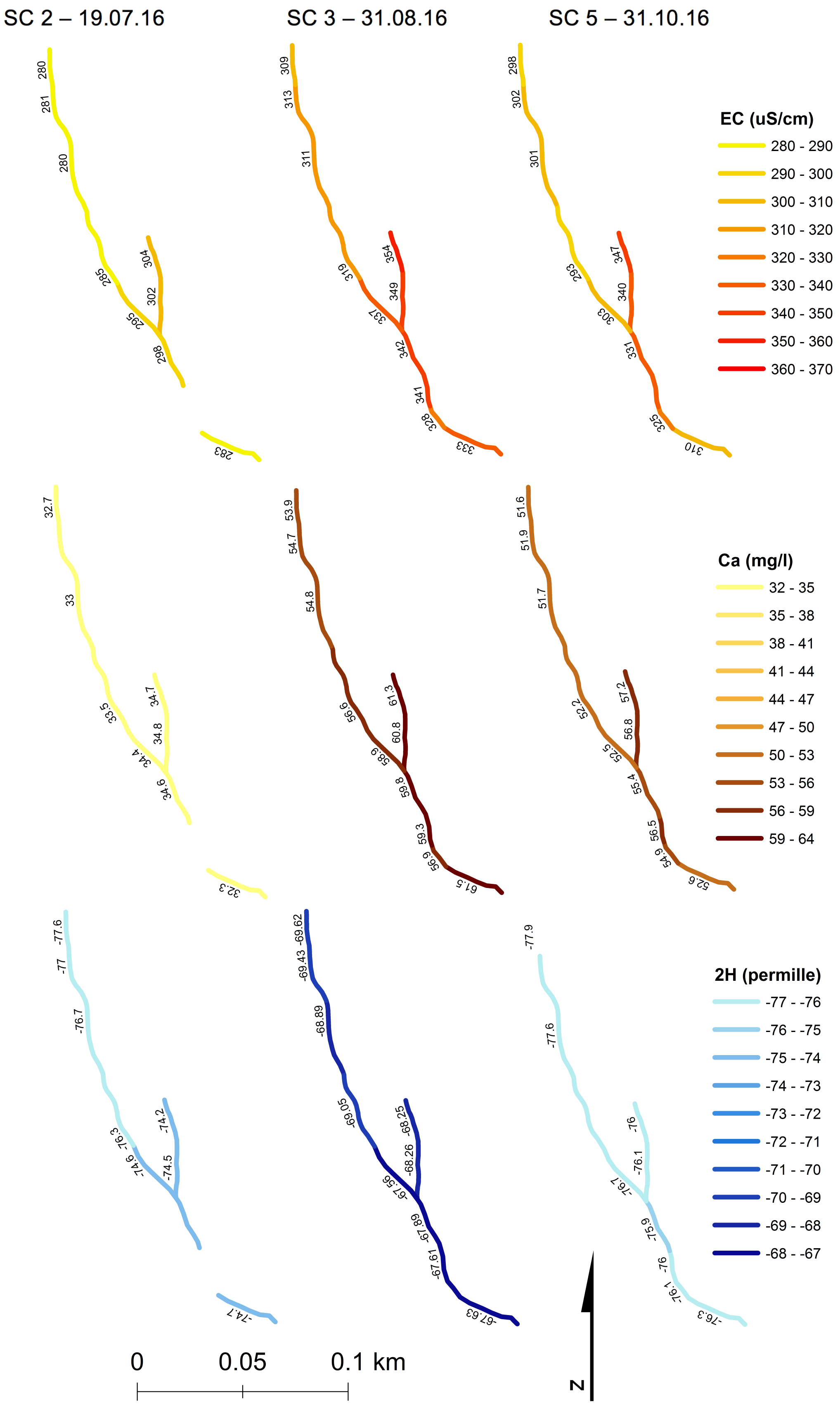


Figure 25: Maps of EC, Ca^{2+} concentration and δ^2H (top to bottom) along stream branches in **C21** measured in SC2, SC3 and SC5 (left to right). The maps of SC 4 are displayed in the results section (Chapter 4).

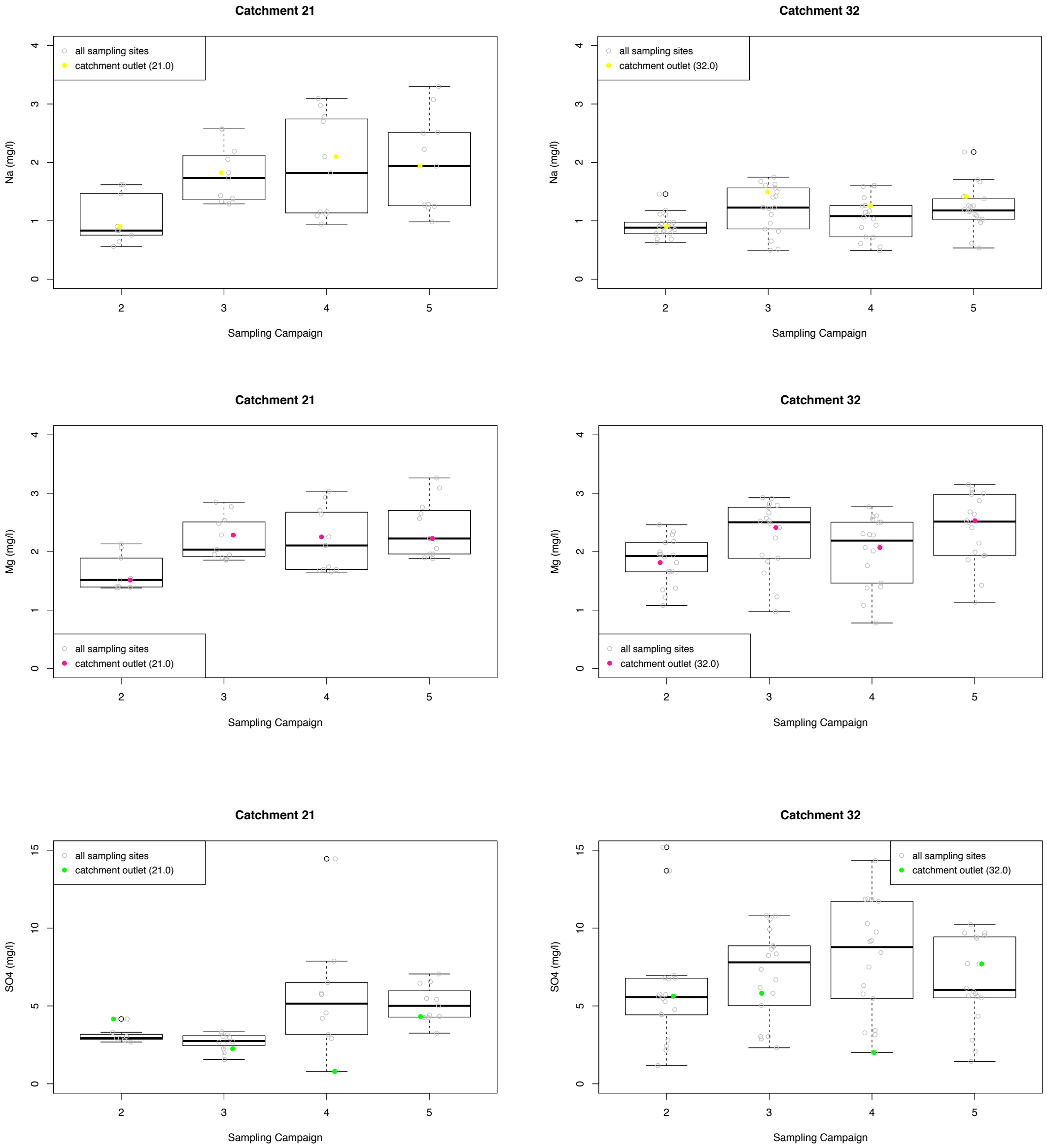
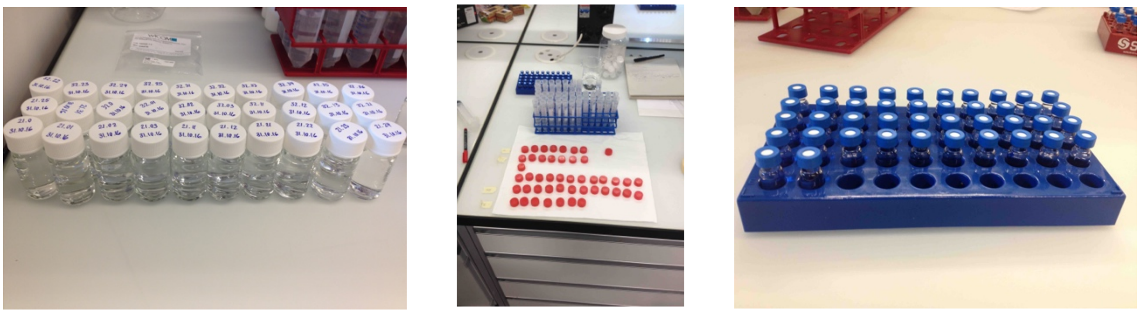


Figure 26: Boxplots, comparing all stream Na^+, Mg^{2+} and SO_4^{2-} concentrations with the concentrations measured at the catchment outlet (21.0 in C21 and 32.0 in C32) per SC.

Appendix C: Pictures of field and laboratory work

Picture 1: marking of the sampling locations with flags

Picture 2: field preparation of sampling bottles and fieldbook.



Picture 3: sample separation for isotope- (left), cation- (middle) and anion analysis (right).

Picture 5: field equipment for ground- and streamwater measurements (left) and for salt tracer measurements (right).

Picture 6: runoff (v-notch weir) of C32 (left) and view from C32 (right)

Appendix D: 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.

Zürich, 30 June 2017 Nadja Rebecca Grunder