We appreciate the helpful comments of the reviewers and editor. Please find below in blue font, the summary of how we have addressed each review comment in the revised manuscript. The line numbers in the responses refer to the revised manuscript.

Reviewer #1

This paper investigates spatio-temporal variability of end-member chemistry in a mountainous catchment. In a second step, EMMA is performed for four runoff events determining that soil sources contribute in addition to baseflow and precipitation, but groundwater being the dominating component. Additionally, the authors tested whether concentration of geochemicals could be calculated from conservative mixing. This was not the case. The authors also discussed the potential link between chemistry and changing hydrological connectivity. I find the study and the data set quite interesting. The paper is well written and data analysis is clearly described. While I like to overall paper good, there are several limitations.

We appreciate the overall positive assessment of our work and the helpful suggestions to improve the manuscript.

1. While I like the research questions and the introduction, I do not think that the research gaps for questions 1 and 2 are convincingly presented. For question 3 (first part), I believe that literature shows that this is not the case for most catchment where three component EMMA is performed.

We thank the reviewer for this comment. We recognize that the content and structure of the introduction did not logically lead to the research questions. We changed the introduction such that it provides more background for research questions. We changed the third research question as follows:

"How much do the changes in the concentrations of conservative and non-conservative tracers differ during events and does this difference provide information on the relative contributions of different parts of the catchment and, thus, hydrological connectivity?"

2. The connectivity part is a little bit weak. It is only loosely linked to the results and could be made stronger in results and discussion. The study also lacks a clear definition of hydrological connectivity. Is it mass transport here?

We rewrote the discussion to address this and other comments regarding the discussion. We included more linkages to the connectivity part (various locations in section 5.2 and 5.3), discuss the assumption that a connected water table indicates hydrologic connectivity (L295-300 and L525-531), and highlight points of attention for future connectivity studies (L408-410, L467-469, L531-532).

We agree that defining hydrological connectivity is important and that this will help the reader understand the study better. We now include a definition of hydrologic connectivity in the introduction (L41).

As connectivity here is linked to GW level rising close to the surface. Several recent papers challenged such a simplified assumption (e.g. Jackson et al., 2014, Klaus and Jackson, 2018, Gabrielli and McDonnell, 2020). I guess this is still somewhat in the debate, but clearly data on bedrock permeability should be presented to check whether the assumed connectivity from GW levels can be realistic. Maybe other proof can be provided that GW level can be used to infer connectivity?

To address this question, we now include the following information in the manuscript: "At most locations in the Studibach, there is an almost permanent water table in the low conductivity gleysols. We assume that significant lateral flow occurs when this water table rises into the near-surface layers, where the hydraulic conductivity is much larger (cf. Schneider et al., 2014). Hence, the simulated connectivity refers to groundwater flow in the more permeable layer of the soil, above a saturated soil, and does not consider seepage to the bedrock" (L295-300). We also discuss this assumption and the potential effects of a smaller downslope travel distance due to bedrock seepage on our connectivity simulations (L525-531).

3. While I think that the paper is quite good, the discussion is currently weak. While the authors are discussing the data and their variation in detail (which is appreciated), I miss discussion of the broader impact of the study, as well as a better link to the introduction or the literature in general. Right now, the discussion refers to only a few studies, mainly related to processes in the same catchments. The authors need to present the broader implication of their work, and make their general contribution to the state of the art outside their study site clearer. At the end of the read I was a little unsure on the take home message. I really think the impact of the paper would be much better if that is achieved.

To address the weaknesses indicated by the reviewer, we expanded the discussion and added comparisons to various other studies and study sites (section 5.2 and 5.3). We also addressed the assumptions made to calculate the hydrologically connected area (section 5.3), included a section describing the influence of soil water (section 5.2) and expanded the link to interpretations of hydrologic connectivity (section 5.2 and 5.3). We also added some text to emphasize the take-home messages in the discussion and conclusions.

4. The majority of the figures need to be reworked (3, 5, 6, 8). They lack the quality that is needed for publication.

We revised the color scheme and style of our figures in the manuscript and supplementary material and enlarged all font sizes and points.

We will make sure to fulfil the required DPI when uploading the figures.

Minor comments:

L35: typo "McGuire"

changed

L47: The authors present catchment size and location for the Maimai; one could do the same for the Rietholzbach. The introduction generally good; the research gaps for the first two research question should be made more clear.

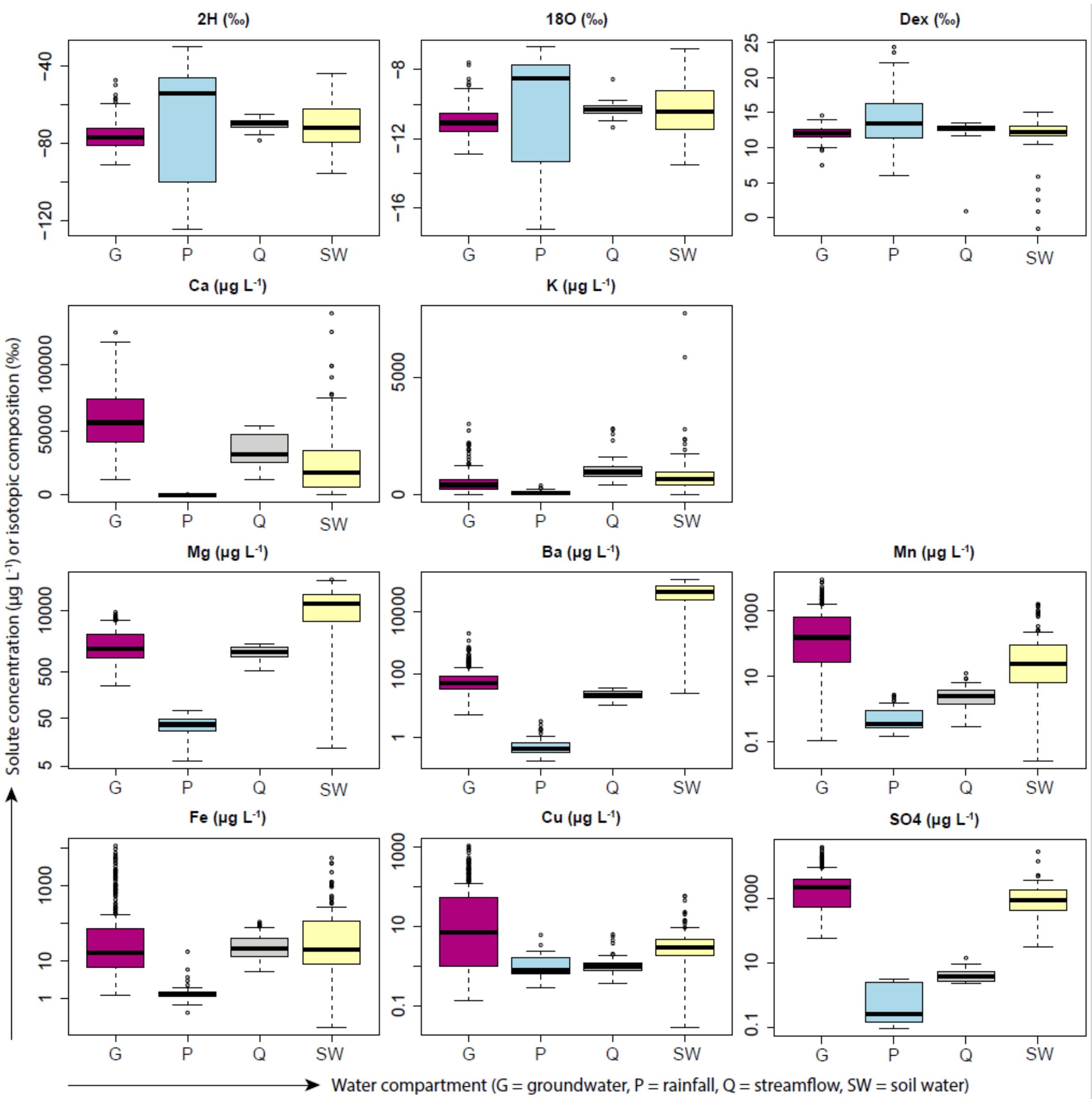
We now mention the catchment sizes and locations throughout the manuscript and adapted the introduction such that the research gaps are presented more clearly.

L92: Why should it only be baseflow? The literature is quite clear that, if tested, this is barely the case. So why asking a question we know to be not true?

We see that our research question could be rephrased to highlight the novelty of our work, rather than the findings from previous studies. As such, we changed the third research question to the following: "How much do the changes in the concentrations of conservative and non-conservative tracers differ during events and does this difference provide information on the relative contributions of different parts of the catchment and, thus, hydrological connectivity?"

L150: That is a valid assumption; but how variable is soil water chemistry (yes, the data is partly presented, but it could be stated)? Additional some more information on the choice of geochemicals and their commonly observed behaviour would be nice.

To address this comment, we included more information on the choice of the solutes (L235-242) and their behaviour in the catchments (L277-284). We stated that the variability in each water source was large (L274-276) and included a figure showing the variability of the various solute concentrations and isotopic compositions in rainfall, groundwater, soil water and streamwater in the supplementary material (S1 in this document, S2 in the manuscript) and refer to this figure in the text (L275 and L378).



S1: Boxplots of the tracer concentrations for the different water types: groundwater (G), rainfall (P), streamflow (Q) and soil water (S). Each boxplot contains all streamflow or rainfall samples taken during the four events or all soil water or groundwater samples taken during the snapshot campaigns used in the study. Units for the isotope tracers are ‰ and for chemical tracers µg L^{-1}. Please note that y-axes differ for each panel, and that the y-axes of the panels on the bottom two rows are logarithmic for better visual comparison.

L188: A clear definition of connectivity is needed, especially when not investigating the mass flux directly.

We agree that adding a definition of connectivity is helpful, and did this in the introduction (L41).

L198/199: You can only assume connectivity in cases where one have a low permeable of underlying bedrock (cf. Jackson et al., 2014; Klaus et al., 2018; Gabrielli and McDonnell, 2020).

We realize that we did not explicitly mention or comment on this assumption and now address it in the methods (L295-300) and the discussion (L525-531).

L219: Define "similar"

The difference in the event water fraction for the two-component hydrograph separation using δ^2H or $\delta^{18}O$ as a tracer was 0.05. We now define this in the methods (L227)

L251ff: There is a nice paper by Harris et al. (1995) that looked into changing end-member contributions. The idea is not too different from the one here.

Thank you for this suggestion. Indeed the paper presents a framework that is interesting for our manuscript. We now mention this paper in the discussion (L538).

L251ff: There is a range of studies that looked (e.g. McCallum et al., 2010), related to hydrograph separation, how GW chemistry is different from baseflow chemistry.

Thank you for recommending this paper. We found that the McCallum et al. (2010)-paper is very interesting, but that its focus on mixing in river-banks does not fit our revised manuscript so well. We found that another paper by the same author (McCallum et al., 2012) fits better to our revised manuscript, and referred to this paper in the discussion (L422-426). We do discuss the influence of mixing processes on the composition of groundwater contributions to the stream. To this end, we refer to the Chanat and Hornberger (2003)-paper, since it is focused more on hillslope-riparian zone mixing (L532-536).

L345: Or does that indicate a much less pronounced connectivity compared to the model?

We appreciate this suggestion and recognize that indeed, a less pronounced connectivity change might also be a valid reason for the smaller change in streamflow composition than expected. We now include this alternative interpretation in the manuscript (L524-525) and also added a more general comparison of the model results and observations to the discussion (L510-540).

L365: Is that surprising? The spatial variability is the maximum extend of the mixing diagram of endmembers. Thus, changes in the stream must be smaller, if the sampling was representative. I am missing the bigger picture here. The discussion is very detailed and evolves around the data being non-conclusive. It would be nice to expand this section and discuss what the key contribution to the field of runoff generation is. How do you go beyond studying this catchment? How does your work related to previous work? What is the key novelty? You may also think of linking your discussion better to the introduction and the used references there.

Indeed, this is not surprising, but very few studies have characterized the spatial variability for groundwater and soil water. We now more clearly mention that this finding can be expected (L398-401), and should be investigated at other sites as well (L408-410).

We addressed the second part of this comment by expanding our discussion with comparisons to the other studies and study sites that were mentioned in the introduction (section 5.2 and 5.3) and including points of attention for future connectivity studies (L408-410, L467-469, L531-532).

L448: but for some? And what do you infer from that?

Indeed, the contribution of soil water is important during some of the events, but not all events. We now discuss the implications of soil water contributions to streamflow in the description of the hydrologic functioning and expanded the discussion on the importance of soil water for hydrologic connectivity studies (L452-469).

Figures 3, 5, 6, 8 are not very well done. While the content is fine, the presentation, choice of colours, font size, and point type should be revised.

Thank you for pointing this out. We adapted our figures as described above.

References;

Chanat, J. G. and Hornberger, G. M., Modeling catchment-scale mixing in the near-stream zone—Implications for chemical and isotopic hydrograph separation, Geophys. Res. Lett., 30, 1091, https://doi.org/10.1029/2002GL016265, 2003.

McCallum, J. L., Cook, P. G., Brunner, P., Berhane, D., Rumpf, C., and McMahon, G. A., Quantifying groundwater flows to streams using differential flow gaugings and water chemistry, J. Hydrol., 416-17, 118-132, https://doi.org/10.1016/j.jhydrol.2011.11.040, 2012.

Reviewer #2

The manuscript entitled "Do streamwater solute cocentrations reflect when connectivity occurs in a small pre-alpine headwater catchment?" by Leonie Kiewiet, Ilja van Meerveld, Manfred Stähli and Jan Seibert, presents an important contribution to the understanding of the hydrological connectivity (or non-connectivity) processes that occur in a pre-alpine catchment, monitored at event scale. The authors presented an exploratory analysis of the hydro-chemical composition of potential water sources and streamflow. They applied widely used, though not so novel, methodologies (simple hydrograph separation and EMMA), but complemented the analysis with hydrological connectivity simulations that make this study interesting. The work is well written, clearly structured and personally enjoyed reading it. Despite the short monitoring period, I find it with potential for publication in HESS after addressing a few suggestions.

We are happy to hear that the reviewer enjoyed reading our manuscript.

The concept of baseflow depends on the method used to estimate it and does not always describe active groundwater flow pathways. I suggest the authors describe what they defined in this study as baseflow

We agree that a definition of baseflow is a useful addition and included the following definition in the methods: "We define baseflow as the streamflow between rainfall-runoff events, and assume that it comes from groundwater" (202-203).

The third objective could be modified, it is well known that baseflow and rain mixture (negligible contribution of soil water) does not explain the changes in solutes concentrations in the streamflow.

We agree that the third question should be modified and changed it as follows:

"How much do the changes in the concentrations of conservative and non-conservative tracers differ during events and does this difference provide information on the relative contributions of different parts of the catchment and, thus, hydrological connectivity?"

One of the principles of EMMA is that it relies on conservative tracers (not involved in adsorption or biological processes) and linear mixing process (Hooper, 2001). Did you analyse the conservative behaviour of the tracers? Please include the tests and state what tracers were used. Also, a graph showing the spatial-temporal concentrations of tracers in water sources would help the reader to contextualize their interaction during events.

We reduced the tracers used in the EMMA so that it only includes conservative tracers. We tested for each tracer if the response was conservative based on the method of Barthold et al. (2011), and describe the test results in the methods (L246-243).

We also added a figure showing the variability in tracer concentrations in the different water sources and streamflow in the supplementary material (S1 in this document, S2 in the manuscript).

Regarding EMMA's analysis, I suggest examining the evolution of events in the PCA space (Inamdar et al. (2013); Barthold et al. (2017); Correa et al. (2018)). Their dynamics and hysteresis can show the proximity of the streamflow to a certain source in the different stages of the event. Although as "soft data" it can bring insights into what groundwater or soil water contributes at a certain time.

We appreciate the suggestion of examining the evolution of events in the PCA space. We now added a panel to Figure 7 and S4 of the revised manuscript that shows the evolution of streamflow during events in the PCA space. From these figures, it is also clear that in the composition of the streamwater samples is very close to the composition of the groundwater samples.

I am concerned about the very high uncertainties (Table 4), 160% in event III and 143% in event IV. Could it be due to the limited streamflow data, input-data uncertainty or time-dependent endmember variability (Chaves et al., 2008; Christophersen and Hooper, 1992). Unluckily end-member solutions do not exhibit low variability compared to the stream chemistry and not exhibit distinctive concentrations between end-members. I encourage the authors to analyse this limitation in more detail. As an alternative the authors could refer to: Phillips, D. L. and Gregg, J. W.: Uncertainty in source partitioning using stable isotopes, Oecologia, 127(2), 171–179, doi:10.1007/s004420000578, 2001, to compute individual uncertainties in the calculation of source contributions to streamflow, this methodology considers the number of samples. The author could identify whether the uncertainties remain very high.

We investigated the high uncertainties that we reported in the previous version of the manuscript. We found a mistake in our uncertainty calculation based on the Genereux (1998) method. We forgot to square a denominator term in the equation. We redid and double-checked all calculations, and the uncertainties are now much lower. We also compared our new results with the uncertainty calculated using the IsoSource mixing model. The uncertainty estimations were within 0.03 of each other, and thus very similar.

We now also calculated the contribution of each source to the total uncertainty. This highlights that most of the uncertainty is due to the uncertainty in the groundwater contributions. We also found that the uncertainty due to the soil water contributions is higher for event II, the only event with considerable soil water contributions than in the other events. We describe these findings in the results (L364-368).

The introduction, methods and results sections are complete and clear to follow, despite some very long sentences that make a little difficult to follow the ideas.

We carefully read through the text and split long sentences.

However, I find the manuscript poorly discussed. The authors support their findings in an extremely local context. The study would benefit from a broader perspective, comparing it with other similar ecosystems and/or with studies of the dynamics of water source contribution streamflow during events for example.

We think that broadening the perspective was indeed helpful. To address this point, we expanded the discussion and added comparisons to other studies and study sites in section 5.2 and 5.3. These cover a range of different ecosystems, some similar, some different to ours.

I assume the figures will be uploaded in a high-quality prior publication. In S1 please include rain and streamflow samples to visualize their distribution (potential streamflow at different colour scale for low, medium and high flows) and check the paper for a few typos.

Indeed, the quality of the figures deteriorated significantly when the file was converted to a .pdf. We will make sure that the final figures are available at the appropriate quality.

We included the rain and streamflow samples in an updated version of supplement S1, and used a different scale for low medium and high flows.

References:

Barthold, F. K., Tyralla, C., Schneider, K., Vaché, K. B., Frede, H.-G., and Breuer, L. (2011), How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis, *Water Resour. Res.*, 47, W08519, doi:10.1029/2011WR010604.

Do streamwater solute concentrations reflect when connectivity occurs in a small pre-alpine headwater catchment?

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Abstract. Expansion of the hydrologically connected area during rainfall events causes previously disconnected areas to contribute to streamflow. If these ~~newly~~ contributing areas have a different hydrochemical composition than the ~~previously~~permanently connected ~~contributing~~ areas, this may cause a change in streamwater chemistry that can not be ~~explained~~described by simple mixing of rainfall and baseflow. Changes in stormflow composition are~~,~~ therefore~~,~~ sometimes used to identify when transiently ~~connected~~disconnected areas (or water sources) contribute to stormflow. We identified the dominant sources of streamflow for four rainfall events in a steep 20-ha pre-alpine headwater catchment in Switzerland ~~and investigated~~to investigate the temporal changes in connectivity ~~for four rainfall events based on streamwater concentrations and groundwater level data~~. First, we compared the isotopic and chemical composition of stormflow at the catchment outlet to the composition of rainfall, groundwater, and soil water. Three-component end-member mixing analyses indicated that groundwater dominated stormflow ~~during all~~for three of the four events, and that soil water fractions were minimal for ~~three of the four~~two events. ~~However,~~Then, we tested whether conservative mixing of rainfall and baseflow could describe the ~~large variability in soil and groundwater~~chemical composition ~~compared to the temporal changes in~~of stormflow ~~composition inhibited the determination of the contributions from the different groundwater sources. Second~~. To this end, we estimated the concentrations of different solutes in stormflow based on the mixing fractions derived from ~~two-component hydrograph separation using~~ a conservative tracer (δ^2H) and the ~~measured~~ concentration of the solutes in baseflow and rainfall. ~~The~~Then, we compared these estimated concentrations to the measured concentrations. We found that the estimated concentrations differed from the measured stormflow concentrations for many solutes and samples. The deviations increased gradually with streamflow for some solutes (e.g., iron and copper), suggesting increased hydrologic connectivity. However, the large variability in soil and groundwater composition compared to the changes in stormflow inhibited the determination of the contributions from ~~riparian and hillslope groundwater with higher concentrations of these solutes, and thus increased hydrological connectivity. The~~the different sources. Our findings ~~of this study~~ show that solute concentrations ~~partly reflect the gradual changes in~~ can be helpful for investigating hydrologic connectivity, and that it is important to quantify the variability in the composition of different source areas.

1 Introduction

During dry periods only a small part of ~~a~~the catchment is connected to the stream, but the connected area can expand dramatically during rainfall or snowmelt events (Stieglitz et al., 2003; Bracken and Croke, 2007; Jencso and McGlynn, 2011; van Meerveld et al., 2015). ~~Knowledge of which areas are connected and contribute to streamflow is important because it helps us to shape our conceptual understanding of how catchments function. For example,~~ For example, Ladouche et al. (2001) showed for the ~~0.8 km^2~~ Strengbach catchment ~~in~~ (France) that the upper layers of saturated areas~~,~~ (2% of surface area, mainly in the lower part of the catchment) contributed up to 30% of the discharge during the initial stages of a rainfall event, ~~even though these areas occupied only 2% of the catchment area. However, during the final stage of an event,~~whereas upslope and downslope ~~areas~~layers contributed equally to flow~~. Similarly,~~ during the final stage of the event. Oswald et al. (2011)~~,~~ showed for a ~~0.8 km^2~~ catchment in ~~north-western~~the Experimental lakes region in northwestern Ontario, Canada, that a large part of the catchment area was hydrologically disconnected from the stream during most events, and that there was a threshold ~~catchment storage at~~after which a larger area contributed to streamflow. Connection of upslope areas does not only lead to large changes in discharge (Lehmann et al., 2007; Detty and ~~McGuire~~Mcguire, 2010~~; van Meerveld et al., 2015~~) but can also cause major changes in ~~streamwater~~stream water composition (e.g., Devito and Hill, 1997; Stieglitz et al., 2003; Ocampo et al., 2006).~~ Interpretations of hydrologic connectivity are often based on such changes in streamwater chemistry (Uhlenbrook et al., 2004; Soulsby et al., 2007; Pacific et al., 2010).~~

~~Hydrologic connectivity, i.e., "the linkage of separate regions of a catchment via water flow" (Blume and van Meerveld 2015) is usually inferred from either stream-based or hillslope-based measurements, because direct observations of connectivity are limited due to the difficulty in observing and quantifying~~Direct observation of hydrologic connectivity is challenging because it is difficult to quantify subsurface processes (Hopp and McDonnell, 2009; Blume and van Meerveld, 2015). Hillslope-stream connectivity can be inferred from hillslope-based measurements or stream-based measurements (Blume and van Meerveld, 2015). Stream-based interpretations of connectivity are usually based on changes in stream chemistry during events. Few studies have compared the results from stream-based and hillslope-based inferences of connectivity. For instance, Burns et al (1998) showed that hillslope contributions to streamflow based on end-member mixing analysis were similar to the subsurface flow measurements for a trenched hillslope. In many studies, conservative tracers (e.g. stable water isotopes or non-reactive elements) are selected to identify the origin of streamflow, using methods such as hydrograph separation (Buttle, 1994) or end-member mixing analyses (EMMA; Hooper et al., 1990; Christophersen and Hooper, 1992). ~~Tracers can also be used to assess connectivity of hillslopes to the streams (Tezlaff et al., 2014; Uhlenbrook et al., 2004). Since stream chemistry is the proportional mixture of all actively contributing areas, quantifying each contribution results in a measure for catchment-wide connectivity. For instance,~~Von Freyberg et al. (2014) used the composition of stormflow during 31 rainfall events and the composition of shallow groundwater to show that streamflow in the Rietholzbach catchment gradually shifted from a riparian-zone composition to a more hillslope-dominated composition as the lower parts of the hillslopes became hydrologically connected to the river network. McGlynn and McDonnell (2003) used ~~silica~~ concentrations of silica and isotope data to show for a 2.6-ha sub-catchment of the Maimai catchment in New Zealand ~~to show~~ that the ~~contributions~~ fraction of water from the hillslopes ~~were~~was larger for an event with higher wetness conditions than for an event with drier initial conditions, and that hillslope contributions were ~~also~~ larger on the falling limb of the hydrograph~~. Several studies in the 31 km^2 Girnock Burn catchment in Scotland investigated connectivity of source areas to the stream using Gran alkalinity and isotope data (e.g., Soulsby et al., 2007; Tezlaff et al., 2014). They found that the upper soil layers and upslope areas increasingly dominated streamflow at higher flows and that the riparian peat soils modulated the streamwater isotopic composition. However, few studies have compared the results from stream-based and hillslope-based inferences of connectivity. Burns et al. (1998) showed that hillslope contributions to streamflow inferred from end member mixing analysis were similar to the subsurface flow measurements for a trenched hillslope~~.

~~Mixing analyses are traditionally performed with conservative solutes and stable water isotopes (Hooper and Shoemaker, 1986).~~ Non-conservative solute concentrations can also provide useful information on hydrological connectivity and flow pathways because they can aid the identification of different source areas (Barthold et al., 2011~~; Abbott et al., 2016).~~). For instance, Soulsby et al. (2008) used Gran alkalinity as a tracer for groundwater and soil water contributions in the Feshie catchment in Schotland. The concentrations of specific elements can also be indicative for differences in redox conditions (e.g., sulfate, iron, manganese), bedrock-contact time (e.g., calcium, magnesium, sodium, barium) or vegetation (e.g., nitrogen, phosphorus, potassium) (Kaushal et al., 2018). ~~It has been suggested that the discrepancy between hydrograph separation results for conservative and non-conservative tracers highlights when and where streamwater is not the result of conservative mixing between end-members, such as baseflow and precipitation (Kirchner, 2003). Instead, it might reflect mixing from~~

different 'old' water sources in the catchment that have different concentrations. Therefore, this discrepancy may provide information on when hillslope-stream connectivity is established. Alternatively, the differences in the relative response of conservative and non-conservative tracers during rainfall events might be (partly) due to reactive processes that mobilize (or immobilize) solutes at the event time-scale (Godsey et al., 2009). As such, focusing on solute responses in stormflow and the difference between conservative and non-conservative tracers might allow us to identify the extent of these reactive transport processes and contributions from 'old' water sources that do not contribute to baseflow.

Solute concentrations in streamwaterstream water might be relatively constant (chemostatic), decrease (dilution) or increase (mobilization) in response to rainfall, depending on the source areas to streamflow and their respective concentrations, as well as reactive transport processes (Godsey et al., 2009; Seibert et al., 2009, Knapp et al., 2020). Godsey et al. (2009) found that concentrations of typical weathering products (calcium, magnesium, silica and sodium) were nearly chemostatic for 59 geochemically diverse US catchments, suggestingindicating that there should be a (constant) source of these solutes. This impliessuggests that the areas that contribute to streamflowconnect during rainfall events have similar concentrations of these solutes as the permanently contributing areas, or higher concentrations to compensate for the dilution caused by the rainfall, or that reactions are fast enough to maintain similar concentrations during the event.

The timing of the onset of contributions from different source areas also affects the solute concentrations (Abbott et al., 2018). Several studies have shown that the relationshiprelation between concentrationsconcentration and dischargestormflow is hysteretic at the event time- scale (e.g., Evans and Davies, 1998; Hornberger et al., 2001). Zuecco et al. (2019) showed that the increase in subsurface connectivity was delayed compared toincreased later than streamflow (anti-clockwise hysteresis) for two sub-catchments of the Studibach catchment in (Switzerland,), suggesting that hillslope runoff may not be thea dominant runoff source at the beginning of rainfall events for these small catchments. IfThis can cause a hysteretic relation between solute concentration and streamflow if hillslope and riparian zone water have a different composition, this can cause hysteresis in the relation between solute concentrations and streamflow. Changes in solute concentrations might also depend on the size of the catchment (Brown et al., 1999) and mixing that occurs during transportmight occur on the way from the source areas to the outlet. For instance, hillslope runoff may bypass the riparian zone through focused locations along the stream channel or via preferential flow pathways (Allaire et al., 2015), and mix with other hillslope sources (Seibert et al., 2009) and riparian groundwater (McGlynn and McDonnell, 2003; Chanat and Hornberger 2003) on its way to the stream.

It has been suggested that the discrepancy between hydrograph separation results for conservative and non-conservative tracers highlights when and where streamwater is not the result of conservative mixing between end-members, such as baseflow and precipitation (Kirchner, 2003). Instead, it might reflect mixing from different 'old' water sources in the catchment that have different concentrations. Therefore, this discrepancy may provide information on when hillslope-stream connectivity is established. Alternatively, these differences might be (partly) due to reactive processes that mobilize (or immobilize) solutes at the event-time scale (Godsey et al., 2009). For all analyses of source areas and connectivity it is important to quantify the variability in the concentrations of conservative and non-conservative tracers because it affects the robustness of the results and thus interpretations of connectivity. However, for most small catchment studies it remains unclear how large the changes in streamwater composition are compared to the spatial variability in groundwater and soil water because the spatial variability in groundwater and soil water are rarely assessed (<10 km^2; Penna and van Meerveld, 2019). As such, focusing on solute responses in stormflow, and the difference between conservative and non-conservative tracers, might allow us to identify the extent of these reactive transport processes, and contributions from 'old' water sources that do not contribute to baseflow.

In this study, we combined spatially distributed soil- and groundwater sampling with event-based streamwater sampling in the pre-alpine Studibach catchment to address the following research questions:

1. How variable is streamwater chemistry during events compared to the spatial variability in soil and groundwater chemistry?
2. What are the dominant sources of streamflow during small to intermediately sized rainfall events?
3. ~~How much do~~ Does conservative mixing of baseflow and rainfall explain the changes in the solute concentrations ~~of conservative and non-conservative tracers differ during events~~or must other sources contribute to stormflow as well? If other sources contribute to stormflow, what are their characteristics and ~~does this difference provide information on the relative contributions of different parts of the catchment and, thus, hydrological connectivity~~when do they contribute to flow?

2. Study catchment

We conducted this study in the ~~0.2 km^2~~20-ha pre-alpine Studibach catchment, a headwater catchment of the Zwäckentobel, located in the Alptal, ~~canton Schwyz,~~ Switzerland. The elevation ~~of the Studibach~~ ranges from 1,270 to 1,650 m above sea level. The mean annual precipitation ~~is~~of about 2,300 mm y^{-1}~~. The precipitation~~ is relatively evenly distributed throughout the year (Feyen et al., 1999), and about one-third falls as snow (Stähli and Gustafsson, 2006). ~~The catchment is steep (average slope: 35°) and characterized by a step-wise topography, with flatter areas and steep slopes due to soil creep and landslides. An open coniferous forest covers about half of the catchment (Hagedorn et al., 2000), a third is characterized as a moor landscape or wet grassland, and the remaining areas are alpine meadows.~~

Streamflow and groundwater levels respond quickly to rainfall (Fischer et al., 2015; Rinderer et al., 2015). The median groundwater level response time is generally less than 30 minutes (Rinderer et al., 2014) and for many events only 3-mm of cumulative rainfall already causes an increase in the groundwater level for a large part of the catchment ~~during typical conditions ((~~Rinderer et al. 2015). ~~The~~Generally, the groundwater level peak ~~precedes the~~preceeds peak discharge in the Studibach at half of the sites, but only by 15 or 20 minutes (Rinderer et al., 2015). Water levels in flatter locations and topographic depressions rise nearly instantaneously, which suggests that they can contribute to streamflow during the early stages of ~~a~~the rainfall event. ~~Previous studies suggest that event~~Event water fractions in stormflow are generally low (Kiewiet et al., in review; von Freyberg et al., 2018), except for events ~~with more than~~exceeding 50-mm of rainfall (Fischer et al., 2017). The catchment is steep (average slope: 35°) and characterized by a step-wise topography of flatter areas and steep slopes due to soil creep and landslides. About half of the catchment is covered by an open coniferous forest (Hagedorn et al., 2000), a third is characterized as a moor landscape or wet grassland, and the remaining areas are alpine meadows.

~~Soils are generally shallow (0.5 m at ridge sites to ~2.5 m in depressions); soil~~Soil depth is weakly correlated to slope (van Meerveld et al., 2018)~~.~~ but generally shallow (0.5 m at ridge sites to ~2.5 m in depressions). The gleysols are underlain by three different types of Flysch bedrock, which is a reworked carbonate rock consisting of deep-water and turbidite deposits. The carbonate-rich bedrock results in high ~~groundwater~~solute concentrations with a calcium-bicarbonate signature, although some sites have high sulfate and magnesium concentrations (Kiewiet et al., 2019).

The Studibach can be subdivided into four different landscape elements with a distinct groundwater composition (Kiewiet et al., 2019 and Fig. 1):

1. Riparian zone, flatter areas and topographic hollows with above-~~-~~ average concentrations of iron and manganese. These areas are from here on referred to as 'riparian';

2. Hillslopes and steeper areas, characterized by above~~-~~ average concentrations of copper, zinc and lead;
3. Areas with above~~-~~ average concentrations of weathering-derived solutes, such as strontium, indicative of longer (and deeper) flow pathways, which are from here on referred to as deep ~~groundwater~~wells;
4. Areas located in a specific part of the catchment that ~~is~~are characterized by high magnesium and sulfate concentrations.

3. Methods

3.1 ~~Hydrometric measurements~~

~~To monitor streamwater and groundwater levels, we used a network of 51 shallow groundwater wells and streamflow gauges (Fig.1) that was installed in 2009–2010 (Rinderer et al., 2014). The wells were distributed based on the topographic wetness index (TWI, Beven and Kirkby (1979)) and cover the range of wet and dry locations in the catchment. All wells were drilled by hand to the bedrock (0.5 to 2.5 m depth), screened over the entire length, except for the top ten centimeters, and sealed with a layer of bentonite clay. Stream stage was measured directly in the stream (outlet; Fig. 1a) or behind a V-notch weir (C5). Water levels were measured at each well and stream location with either a capacitance water level logger (Odyssey Dataflow Systems Pty Limited) or a pressure transducer (DCX-22 CTD Keller AG für Druckmesstechnick or STS DL/N 70, Sensor Technick Sirnach AG). The pressure data were corrected for changes in barometric pressure and temperature using the data from the MeteoSwiss station in Einsiedeln (910 m a.s.l; ca. 10 km from the catchment outlet). Rainfall was recorded at three locations within the catchment with tipping bucket rain gauges (0.2 mm resolution, Odyssey Dataflow Systems Pty Limited; Fig.1a).~~

~~The stream stage data were converted to specific discharge (Q, further referred to as discharge) using a rating curve based on twenty salt dilution measurements. Due to technical issues, there were no observations of stage height at the catchment outlet during events I and II (see section 3.2). We used the correlation between the specific discharge at the catchment outlet and an intermediately sized sub-catchment (C5, Fig.1a) for the four months following events I and II to estimate the streamflow at the outlet for the period without data (coefficient of determination r^2 = 0.66, RMSE = 0.75 mm h^{-1}, for comparison the 10^{th} and 90^{th} percentile of Q at the catchment outlet for this period were 0.35 and 2.11 mm h^{-1}, respectively). We assume that the uncertainty in the discharge for events I and II does not affect our conclusions as they are largely based on relative changes in streamflow during the events. The ranking of the events based on the peak of the (reconstructed) discharge was the same as the ranking based on the peak rainfall intensity.~~

~~3.2~~ Sample collection

We analysed the streamflow and stream chemistry for four events (I-IV; Table 1) in ~~the~~ fall ~~seasons of~~ 2016 and 2017. Stream water samples were collected at the outlet of the Studibach using automatic samplers (full-size portable sampler, 3712, ISCO Teledyne, USA). The sampling interval was based on the ~~expected~~predicted event duration. The multi-interval program was set to sample streamwater every ten to twenty minutes at the start of the rising limb (maximum of six samples). The remaining eighteen samples were taken at an hourly-interval. We emptied the samplers within 24 hours after sample collection to avoid fractionation. We used a timer to start the sampler if the ~~expected~~predicted time of the onset of the rainfall was during the night. Rainfall was collected with passive sequential samplers (built after Kennedy et al. (1979), and described in detail in Fischer et al. (2019)) at two locations in the catchment (rain gauge location one and two in Fig. 1a). The samplers collected a sample for approximately every 5 mm of rainfall.

For soil water and groundwater, we used the data from a subset of nine baseflow snapshot campaigns during the snow-free seasonsseason of 2016 and 2017 (Kiewiet et al., 2019). Soil water was collected with six to 18 suction lysimeters at four to six sites (at 15, 30 and 50 cm below the surface at forested and non-forested sites at three different elevations: 1361, 1502, 1611 m a.s.l.; Fig.1a). We applied a tension of 50 mbar to the lysimeters and collected the soil water sample the next day. Groundwater was collected at all wells that contained water (34 to 38 wells). The shallow wells were either purged or at least twice the well volume was extracted a day before the sampling. For a detailed description of the groundwater sampling procedure, see Kiewiet et al. (2019).

Ideally we would use the soil water and groundwater samples taken right before the rainfall events, but these data are not available. Instead, we have data from sampling campaigns two to nine days before (event II) or after the events (I, III and IV). Since the spatial variability in groundwater composition in the Studibach is larger than the temporal variability (Kiewiet et al., 2019), we assume that the groundwater and soil water samples reflect the typical composition (and variability) of soil water and groundwater, although absolute concentrations might have been slightly different. A Principal Component Analysis (PCA) on the chemical and isotopic composition of all groundwater (n=335) and soil water (n=116) samples (z-transformed) showed that these were consistently different in the principal component space; only six of the soil water samples (5%) plotted within the same area as the groundwater samples (see S1 for the PCA result and Table 2 for the average concentrations).

3.32 Sample analyses

The samples for cation and anion analyses were stored in athe fridge (6 °C) before lab analyses (within a few days) or were frozen (-18 °C) directly after collection until shortly before the analyses. The samples were filtered (0.45 µm; SimplepureTM Syringe Filter) and acidified (only for cation analysis) to mobilize trace metals. The samples , and were analysed at the Physics of Environmental Systems laboratory at ETH Zurich. We used an ion-chromatograph (861 Advanced Compact IC, Metrohm) for anions and a mass-spectrometer (ICP-MS 9700, Agilent technologies) for cations. Calibration curves were obtained from measurements with five calibration standards before or after measuring the samples.

(Switzerland) using an ion-chromatograph (861 Advanced Compact IC, Metrohm) for anions and a mass-spectrometer (ICP-MS 9700, Agilent technologies) for cations. Calibration curves were obtained from measurements with five calibration standards before or after measuring the samples.

The samples were analysed for stable water isotope composition with a cavity ring-down spectroscopeCavity Ring-Down Spectroscope (L2140-I (CRDS) or L2130-I (CRDS), Picarro, Inc., USA) at the Chairs of Hydrology at the University of Freiburg (Germany). The), with a reported precision isof ± 0.16 ‰ for $\delta^{18}O$ and ± 0.6 ‰ for $\delta^{2}H$. All samples plotted close to the local meteoric water line. The average (± standard deviation) of the Line Conditioned-excess (LC-excess; Landwehr and Coplen (2006)) for all 516 stream-, soil- and groundwater samples was 5.3 ± 1.3 ‰, excluding five soil water samples (taken at 15 (three samples), 30 (one sample) and 50 (one sample) cm below the soil surface) for which LC-excess ranged from –9.6 to -1.5 ‰. Deuterium-excess (D_{ex}) was calculated as $D_{ex} = \delta^{2}H - (8 \cdot \delta^{18}O)$.

3.3 Hydrometric measurements

To monitor streamwater and groundwater levels, we used a network of 51 groundwater wells and seven streamflow gauges (Fig.1) that were installed in 2009–2010 (Rinderer et al., 2014). The wells were distributed based on the topographic wetness index (TWI, Beven and Kirkby (1979)) and cover the range of wet and dry locations in the catchment. All wells were drilled by hand to the bedrock (0.5 to 2.5 m depth), screened over the entire length except for the top ten centimeters, and sealed with a bentonite clay. Stream stage was measured directly in the stream (C6 and outlet; Fig. 1a), behind V-notch weirs (C3, C4, and

C5) or in H-flumes (C1 and C2). Water levels were measured at each well and stream location with either a capacitance water level logger (Odyssey Dataflow Systems Pty Limited) or a pressure transducer (DCX-22 CTD Keller AG für Druckmesstechnick or STS DL/N 70, Sensor Technick Sirnach AG). The pressure data were corrected for changes in barometric pressure and temperature using the data from the MeteoSwiss station in Einsiedeln (910 m a.s.l; ca. 10 km from the catchment outlet). Rainfall was recorded at three locations within the catchment with tipping bucket rain gauges (0.2 mm resolution, Odyssey Dataflow Systems Pty Limited; Fig.1a).

The stream stage data were converted to specific discharge (Q, further referred to as discharge) using a rating curve based on twenty salt dilution measurements. Due to technical issues, there were no observations of stage height at the catchment outlet during events I and II. We used the correlation between the specific discharge at the catchment outlet and an intermediately sized sub-catchment (C5, Fig.1a) for the four months following events I and II to estimate the streamflow at the outlet for the period without data (coefficient of determination $r^2 = 0.66$, RMSE = 0.75 mm h^{-1}, for comparison the 10th and 90th percentile of Q at the catchment outlet for this period were 0.35 and 2.11 mm h^{-1}, respectively). The ranking of the events based on the peak amount of the (reconstructed) discharge was the same as the ranking based on the peak rainfall intensity, and we therefore assume that the uncertainty in the discharge for events I and II does not affect our conclusions.

3.4 Groundwater-level-based connectivity assessment

We investigated if the assumption of conservative mixing breaks down at a certain specific discharge or hydrologic connectivity. To this end, we related the ratio of the estimated and measured concentrations (C_{Q_x}/C_{es_x}, see 3.5.3) for each solute to the discharge and the calculated fraction of the cachment that was connected to the stream. We used the data-driven model of Rinderer et al. (2019) to determine which parts of the catchment were active and connected to the stream. This model uses the water level data from all 51 wells in the catchment and time series clustering to assign each pixel in the catchment to one of six groundwater level clusters. For each time step, the average relative groundwater level for all monitored wells that belong to a cluster is calculated and assigned to all pixels in that cluster. This relative water level is then transformed to an absolute water level based on the correlation between soil depth and slope. If the water level is within 30 cm of the soil surface (i.e., the part of the soil where the hydraulic conductivity is high), the pixel is considered active, otherwise it is considered inactive. If a pixel is active and, based on surface topography, connected to the stream via other active pixels, it is assumed to be connected to the stream. Rinderer et al. (2019) tested the sensitivity of this method for misclassification of the clusters by randomly re-assigning pixels to different clusters and for the uncertainty in the soil depth by comparing the connectivity timeseries to the timeseries computed with a DEM-based soil map. The soil depth had only minor influence on the model results (RSME > 0.0003% of the relative soil depth), wheareas cluster misclassifications could result in up to 8% difference in the modeled connected area between the different model runs.

3.5 Data analysis

We investigated the sources of streamflow using two and three-component mixing analyses, and investigated the difference between the observed solute concentrations and those estimated assuming linear mixing of baseflow and rainfall. We examined the changes in streamwater concentrations during the rainfall events using concentration-discharge (C-Q) relationships, and identified the corresponding hysteresis index (Zuecco et al., 2016). For this, we normalized both the discharge and the concentrations so that zero represents the smallest measured value, and one the highest measured value.

We used Mann-Whitney U tests to determine if the median concentrations of different (ground)water types were significantly different (Table 2). We pairwise tested seven groups: all groundwater, riparian groundwater, hillslope

groundwater, all soil water, soil water at forested sites, soil water at non-forested sites, and rainfall. We found that the soil water samples taken at forested or non-forested sites were never significantly different, and thus merged these data.

3.4 Data analysis

3.4.1 Relative concentrations

We examined the changes in streamwater concentrations during the rainfall events using concentration-discharge (C-Q) relationships and identified the corresponding hysteresis index (cf. Zuecco et al., 2016). For this, we normalized both the discharge and the concentrations so that zero represents the smallest measured value, and one the highest measured value.

For each solute, we calculated the relative concentration R_x by comparing the concentration of the sample to that of baseflow:

$$R_x = \frac{C_{Q\_x}}{C_{BF\_x}} \quad (2)$$

Where C_{Q_x} and C_{BF_x} are the concentration of solute x in streamwater during the event and in baseflow before the event. We define baseflow as the streamflow between rainfall-runoff events and assume that it comes from groundwater. The relative concentration indicates dilution (R_x<1) or enrichment (R_x≥1)) during the events. It thus quantifies the direction and magnitude of the change in solute concentrations (note that R_x is not an alternative measure for the fraction of baseflow in stormflow). We used the relative concentrations (R_x, Eq. 2) to identify groups of solutes using hierarchical cluster analysis.

3.4.2 Hydrograph Separation and End-Member Mixing Analysis

We tested if the median concentrations of different (ground)water types were significantly different (Table 2; Tukey-Kramer test; Tukey.HSD in the 'agricolae' R-package). We pairwise tested seven groups: all groundwater, riparian groundwater, hillslope groundwater, all soil water, soil water at forested sites, soil water at non-forested sites, and rainfall. We performed all computations in R (R core team, 2013) and used a 95-percent confidence interval for all statistical tests. We found that the soil water samples taken at forested or non-forested sites were never significantly different, and thus merged these data.

We investigated the sources of streamflow using two and three component mixing analyses and investigated the difference between the observed solute concentrations and those estimated assuming linear mixing of baseflow and rainfall. Ideally, we would use the soil water and groundwater samples taken directly before the rainfall events, but these data are not available. Instead, we have data from sampling campaigns two to nine days before (event II) or after the events (I, III and IV). Since the spatial variability in groundwater composition in the Studibach is larger than the temporal variability (Kiewiet et al., 2019), we assume that the groundwater and soil water samples reflect the typical composition and variability of soil water and groundwater, but acknowledge that absolute concentrations might have been slightly different. A Principal Component Analysis (PCA) on the chemical and isotopic composition of all groundwater (n=335) and soil water (n=116) samples (z-transformed) showed that soil water and groundwater were consistently different in the principal component space; only six of the soil water samples (5%) plotted within the same area as the groundwater samples (see S1 for the PCA result and Table 2 for the average concentrations).

We used R (R Core Team, 2013) for all data analyses, and a significance level of 0.05.

3.5.1 Hydrograph Separation and End-Member Mixing Analysis

We estimated the fraction of event (f_e) and pre-event (f_{pe}) water in the streamwaterstream water samples (C_t) using two-component isotope hydrograph separation (Eq. 1). The results for δ^2H and δ^{18}O were similar (difference between the event-average f_{pe} ≤ 0.05). Becausebut because the ratio of precision to range was better for δ^2H, we report only the δ^2H results. A pre-event baseflow sample was used to characterize the pre-event water composition (C_{pe}~~). The~~), and the incremental weighted mean of rainfall was used to characterize the event-water composition (C_e).

$$f_{pe} = \frac{C_t - C_e}{C_{pe} - C_e} \qquad (1)$$

We also estimated the fractions of groundwater, soil water and rainwater in each streamwater sample, using a three-component End Member Mixing Analysis (EMMA; Christophersen and Hooper (1992)). We based the EMMA on the first two principal components of a PCA that included ~~all conservative tracers. We considered a tracer conservative if the concentration was linearly correlated to that of at least one other tracer (cf. Barthold et al., 2011). To determine~~ the isotopic composition and the ~~conservativeness, we used all groundwater,~~solutes for which the concentrations in stormflow differed from the concentrations in soil water and ~~streamwater samples used in this study (n=549), and set the threshold for a linear correlation to $R^2 \geq 0.5$ and $p < 0.01$. EC,~~ groundwater (barium, calcium, magnesium, ~~barium, δ^{2}H~~potassium and ~~δ^{18}O~~sulfate) or which were ~~conservative based on this definition; the other tracers (e.g.,~~ different for the different groundwater types (copper, ~~sulfate, potassium,~~manganese and iron~~) were not. However, note that this threshold does not per se imply a linear trend and that although a linear trend is consistent with conservative mixing, it does not necessarily confirm conservative mixing either (James and Roulet, 2006).~~).

We used a Gaussian error-propagation method (Genereux, 1998) to estimate the uncertainty in the calculated fractions of ~~the~~ source waters for the two-component hydrograph separation and EMMA. For the two-component hydrograph separation~~,~~ we defined the uncertainty in the event and pre-event water composition as the standard deviation of the rainfall sampled during the event, and groundwater sampled during the snapshot campaign closest to the event (see Table 1), respectively. For the uncertainty in the EMMA, we used the standard deviation of groundwater, soil water and ~~rainwater~~rain water samples that were used for ~~the~~this particular event. We used the laboratory accuracy for the uncertainty of the streamwater samples in the two-component hydrograph separation, and ~~for the EMMA~~ assumed that the uncertainty for the streamwater samples in the principal component space was ~~similar to the standard deviation of the last three streamwater samples taken during each event (i.e. the last streamflow samples taken at the falling limb of the hydrograph). We multiplied the standard deviation with a t-value based on the number of samples and used a 95-percent confidence interval for all uncertainty estimations.~~ minimal.

3.5.2 Relative concentrations

For each solute, we calculated relative concentration R_x by comparing the concentration of the sample to that of baseflow:

$$R_x = \frac{C_{Q\_x}}{C_{BF\_x}} \qquad (2)$$

Where C_{Q_x} and C_{BF_x} are the concentration of solute x stream water during the event and in baseflow before the event. The relative concentration indicates dilution (R_x <1) or enrichment (R_x ≥1)) during rain events and thus quantifies the direction and magnitude of the change in solute concentrations (note that R_x is not an alternative measure for the fraction of baseflow in stormflow).

We used the relative concentrations (R_x, Eq. 42) to identify groups of solutes by hierarchical clustering. We then compared the relative concentrations of each solute to that of a conservative tracer to determine any deviation in the relative concentration from conservative mixing between baseflow and rainfall.

3.5.3 Deviation of concentrations from mixing of baseflow and rainfall

~~We~~The expansion of hydrologically connected areas during events can cause source waters that did not contribute to baseflow to contribute to stormflow. This violates the assumption of simple conservative mixing if baseflow is used to represent the 'old' water (e.g., Hooper, 2001). We therefore compared the measured streamflow concentrations for each solute to the concentration that would be expected based on conservative mixing of rainfall and baseflow ~~(C_{es}):~~using the pre-event water fraction calculated for δ^2H (C_{es}):

$$C_{es\_x} = \left(C_{BF\_x} \cdot f_{pe}\right) + \left(C_{P\_x} \cdot (1 - f_{pe})\right) \quad (3)$$

where C_{es_x} is the 'estimated' concentration for solute x, C_{BF_x} and C_{P_x} are the concentrations for solute x in baseflow and rainfall (average rainfall composition: Table 2), and f_{pe} is the pre-event water fraction for that sample, as determined from the two-component hydrograph separation ~~using~~based on δ^2H ~~as the tracer~~ (Eq. 1).

We ~~compared~~investigated the relation between discharge and the potential contribution of different source areas by comparing the estimated (C_{es_x}) and measured streamflow (C_{Q_x}) concentrations for each sample and solute ~~to assess the relationship between discharge and the potential contribution of different source areas~~. We assumed that overestimation of the concentrations ($C_{Q\_x}/C_{es\_x} > 1$) indicates either a contribution from source areas that were not connected during baseflow and have a higher concentration than the sources that contributed to baseflow, or reactive transport. Similarly, underestimation of the concentrations ($C_{Q\_x}/C_{es\_x} < 1$) indicates either a contribution from source areas that ~~did~~were not ~~contribute~~active during baseflow and have ~~a~~ lower concentration than the sources that contributed to baseflow~~,~~ or reactive transport. Given the characteristic concentrations in different (ground)water types (Table 2 and ~~3,~~ Fig. 2), we ~~interpret the changes in the streamwater composition during an event as following: 1)~~ assume that higher copper ~~and nickel~~ concentrations are indicative of flow from hillslopes and forested areas, ~~2)~~ higher iron and manganese concentrations are indicative of ~~flow~~larger contributions from riparian areas, ~~3)~~and higher D_{ex}~~,~~ or barium~~, magnesium~~ and chloride concentrations are indicative of soil water~~, 4)~~ (Fig. 2). Lastly, higher potassium concentrations can indicate either soil water or hillslopes ~~groundwater. However, note that the variability for soil water, groundwater and rainfall was large (Table 2, and see supplement S2 for boxplots of tracer concentrations in each water compartment). Also, the non-conservative nature of these tracers should be taken into account. For instance, iron and manganese are mainly soluble under anoxic, reducing conditions, such as in the riparian areas, but they might oxidize and form an insoluble compound after entering the streams. Adsorption of metals (e.g., iron, copper, zinc) to organic compounds or clay particles may also influence the concentrations in streamflow, and their concentration may be underestimated if they are adsorbed to coarser particles~~contributions, even though we recognize that ~~settle out during streamflow recession (Kaushal~~potassium also has a geogenic origin and ~~et al., 2018). The concentration of some solutes~~ is~~, furthermore, controlled by weathering processes or~~ influenced by ~~plant uptake because they are macro (potassium, magnesium) or micro (e.g., copper, nickel) plant nutrients. In this study, we assume that concentration increases or decreases due to weathering or plant uptake are negligible at the event (i.e., hourly) time scale.~~

~~**3.4.4 Groundwater-level-based connectivity assessment**~~

~~We investigated in how far stream chemistry reflects conservative mixing of baseflow and precipitation and whether this breaks down at a certain specific discharge or reflects an increase in hydrologic connectivity. We related the ratio of the estimated and measured concentrations (C_{Q_x}/C_{es_x}, see 3.4~~biological processes.~~3) for each solute to the discharge and the calculated fraction of the cachment that was connected to the stream. We used the data-driven model of Rinderer et al. (2019) to determine which parts of the catchment were active and connected to the stream. This model uses the water level data from all 51 wells in the catchment and time series clustering to assign each pixel in the catchment to one of six groundwater level~~

~~clusters. For each time step, the average relative groundwater level for all monitoring wells that belong to a cluster is calculated and assigned to all pixels in that cluster. This relative water level is then transformed into an absolute water level based on the correlation between soil depth and slope. If this simulated water level is within 30 cm of the soil surface (i.e., the part of the soil where the hydraulic conductivity is high), the pixel is considered active, otherwise, it is considered inactive. If a pixel is active and, based on surface topography, connected to the stream via other active pixels, it is assumed to be connected to the stream. We thus assume that significant lateral flow occurs when the water table rises into the near-surface layers, where the hydraulic conductivity is much larger (cf. Schneider et al., 2014). Hence, the simulated connectivity refers to the connectivity of groundwater flow in the more permeable layer of the soil above the more permanently saturated soil. In the Studibach, there is an almost permanent water table in the low conductivity gleysols in most locations. It is thus not so likely that the lateral water flow would infiltrate into the bedrock before reaching the stream (Jackson et al., 2014). Rinderer et al. (2019) tested the sensitivity of the method for misclassification of the clusters by randomly re-assigning pixels to different clusters and the uncertainty in the soil depth by comparing the connectivity time series to the time series computed with a different (DEM-based) soil depth map. The soil depth had only a minor influence on the model results (RSME > 0.0003% of the relative soil depth). Still, misclassification of pixels (i.e., assigning them to a different cluster) could result in up to an 8% difference in the simulated connected area between the different model runs~~.

4. Results

4.1 Event characteristics

Total rainfall for the four events ranged between 17 and 33 mm (Table 1, Fig. 3). ~~The duration of the events ranged from 7 to 27 hours. The four~~All events were larger than the long-term average in daily precipitation and within the upper ~~30th percentile~~30% of daily precipitation at the long-term meteorological station Erlenhöhe, located 500 meters from the catchment outlet (median: 10.0 mm; mean ± sd: 14.1 ± 13.8 mm for all 7452 days with more than 1 mm of precipitation between 1981-2017; Stähli, 2018). However, ~~the events~~they were smaller than the 50 mm threshold for large event-water contributions ~~of event-water to streamflow~~ (Fischer et al. 2017). The duration of the events ranged from 7 to 27 hours. The average and maximum 10-minute rainfall intensities ranged between 1.2 and 3.9 mm h^{-1} and between 4.8 and 22.8 mm h^{-1}, respectively.

Discharge at the catchment outlet increased the least (~~from~~ 0.02 to 0.07 mm h^{-1}) for the smallest event (I), and most for event III (0.08 to 0.43 mm h^{-1}). The ~~simulated~~modelled fraction of the catchment that was hydrologically connected ~~to the stream~~ varied from 0.27 (before the start of ~~events~~event I and II) to 0.68 (~~at the time of~~ during peak flow ~~for~~of event III) (Fig. 4). The relation between the ~~simulated~~ fraction of the catchment that was connected to the stream and discharge was non-linear for all events (Fig. 5, top row). ~~For all of the four events, connectivity was lower on the rising limb of the hydrograph than on the falling limb for the same discharge.~~ For event I~~,~~ the connected area increased significantly at the recession of the streamflow~~.~~ ~~For~~, whereas for event II connectivity increased little during the sampling period (0.27 to 0.28). ~~Discharge~~Interestingly, discharge increased to >4 mm h^{-1} after the sampling period of event II due to additional rainfall, ~~but interestingly the simulated~~whereas connectivity increased only marginally (up to 0.35; see ~~S3) during this period.~~S2). During ~~the smaller events with initially~~these periods of relatively low connectivity, the hydrologically connected area extended laterally from the stream up, but remained confined to the flat areas. For the intermediate events (III and IV), the lateral extension was larger~~,~~ and parts of the hillslopes became connected. However, the data~~-~~ based model suggested that during all ~~four~~ events, large parts of the catchment remained hydrologically disconnected ~~from the stream network~~ (Table 1~~, Fig. 4~~).

4.2 Concentration-discharge relationships

The chemical and isotopic composition of streamwater changed during all ~~four~~ events, but the magnitude and direction of the response differed for each event and solute (Fig. ~~5).~~5). The change in the concentrations was smallest during event I (e.g., a maximum change of 7.7 mg L^{-1} for Ca and 15.8 µg L^{-1} Fe) and largest for event III (a maximum change of 39 mg L^{-1} and 72.9 µg L^{-1} for Ca and Fe, respectively). Hysteresis in the relation between solute concentrations and discharge depended on the event size and differed between solutes (Table 3, Fig. 5). During ~~events~~event III and IV~~,~~ the relation between discharge and concentration was hysteretic for most solutes. The double discharge peaks during events I and II (Fig. 2) resulted in a double loop in the concentration discharge relationship for deuterium~~, iron,~~ and ~~calcium~~iron (Fig. 5).

The average relative concentration (average R_x for all the ~~streamflow~~ samples ~~taken during the~~from all four events, n=100, Eq. 2) for deuterium excess (D_{ex}) and chloride were 4.1 and 2.0, respectively. This reflects the substantial increase in these concentrations during events. Manganese and iron concentrations also increased with increasing discharge, but less than D_{ex} and chloride (mean R_x: 1.0 for both iron and manganese; maximum R_x: 2.8 and 3.2, respectively). On average, the concentrations of copper, nickel and zinc decreased with increasing discharge (mean R_x: 0.78, 0.63 and 0.31), but individual stormflow samples were enriched up to 1.7, 1.3 and 1.1 times the baseflow concentration, respectively. Concentrations of iron and copper were always higher on the falling limb than on the rising limb (counter-clockwise hysteresis). Event I was the only event during which copper concentrations did not increase ~~with increasing discharge.~~ from the baseflow concentration.

The concentrations of sodium, magnesium, calcium and barium decreased with increasing discharge (mean R_x: < 0.77). The concentrations of these solutes, and also sulfate, were higher on the rising limb than on the falling limb (resulting in clockwise hysteresis). Sulfate concentrations decreased with increasing discharge during events I, III and IV but increased with discharge during event II. Potassium and sulfate concentrations (range R_x: 0.2–1.7 and 0.3–1.4, respectively~~)~~), were highest shortly after the onset of an event (first four samples~~)~~), and decreased afterwards. These differences in the magnitude and timing of the change in solute concentrations and isotopic composition allowed for subdivision of the ~~tracers~~solutes into different groups (A to D; Table 3, Fig. 6) based on the computed R_x values for all events~~ (A to D; Table 3, Fig. 6).~~.

4.3 Hydrograph ~~separation~~Separation and End Member Mixing Analysis~~ results~~

Two-component hydrograph separation results indicated that most stormflow was 'old' water (Fig. 3; Table 3). The maximum event water fraction (f_e) was highest for event II (f_e = 0.24±0.~~61~~31) and smallest for event IV (f_e = 0.~~14~~03±0.~~28). However, the differences between the events were much smaller than the associated uncertainties (Table 4~~19). The high event water fraction of event II occurred when the connected area was relatively small. The fraction of connected area during event II expanded only 0.01 (up to 0.28) during the period that we sampled (see ~~S3).~~ S2). The high event-water fractions for event III, compared to the similarly sized event IV, might be the result of the much smaller hydrologically connected area and relatively high peak rainfall intensity ($I_{p\text{-}max}$: 24 mm h^{-1} vs 10 mm h^{-1} for event IV, Table 1).

The explanatory power of the first two principal components, for all stormflow, soil water and groundwater samples was 41.9% for event I (PC1: 26.0%; PC2: 15.9%) and 43.2% for event III (PC1: 27.0%; PC2: 16.2%; Fig. 7a and c). For event II and IV the explanatory power was 41.1% and 49.0%, respectively; see S3). The principal component axes were most strongly determined by the calcium concentrations (orientation close to PC1 for both events), the isotopic composition (more so in event III) and to a lesser extent concentrations of copper, magnesium, potassium, and deuterium-excess (Fig. 7a and c). It was possible to calculate the relative fractions of groundwater, soil water and rainwater in stormflow for all events ~~based on EMMA as well~~ but the calculated uncertainties were very large (Table 4). Groundwater ~~dominated streamflow during all events~~fractions (f_{GW}) were larger than rainwater and soil water fractions for events I, III and IV (range f_{GW}: 0.~~49±0.14 to~~

0.81±0.19). The event39±1.59 to 0.72±1.43). During event II, the rainwater fraction was largest (fraction rainwater: 0.45±0.60; soil water: 0.33±0.60; groundwater: 0.21±0.60). Event-average soil water fraction was considerable during event II (f_{SW}: 0.27), but fractions were negligible (f_{SW} ~0) during the other events (f_{SW}: ~0I and IV (Table 4). The event-average pre-event water fractions based on the EMMA (i.e., end-member mixing analysis (the sum of the groundwater and soil water fractions) were similar towas lower than the pre-event water fractionsfraction estimated using δ^2H as a tracer in the two-component hydrograph separations (range f_{GW} + f_{SW}: 0.7354 to 0.8177 vs range f_{pe}: 0.76 to 0.86). Although the results were similar, the uncertainties for EMMA were smaller than for the two-component hydrograph separation. The uncertainties for the EMMA results were mainly caused by the uncertainty in the groundwater fraction (contribution of the groundwater uncertainty to the total uncertainty: 97%, 50%, 94%, and 94% for events I-IV, respectively). This is due to the large contribution of groundwater to streamflow and the large spatial variability in the groundwater composition. For event II, the uncertainty due to the soil water contributions was larger than for the other events (25% for event II vs. 0.01%, 3% and 5% for event I, III and IV, respectively).

The explanatory power of the first two principal components for all stormflow, soil water and groundwater samples was 76.3% for event I (PC1: 53.1%; PC2: 23.2%) and 82.0% for event III (PC1: 56.2%; PC2: 25.8%; Fig. 7a and c). For event II and IV the explanatory power was 72.6% and 83.8%, respectively (see S4). The most striking aspect of the mixing plots, however,The most striking aspect of the mixing plots is the small change in the composition of stormflow compared to the spatial variation in the composition of the soil and groundwater end-members (Fig. 7b and d). The observed changes in solute concentrations in streamflow were largest during event IIIII (e.g., changes of 2325 µgL^{-1} for Ba; 39 mgL^{-1} for Ca and 115 ‰ for δ^2H) but this change was similar to or smaller than the standard deviation of the concentrations for all the groundwater samples or soil water samples taken during the corresponding snapshot campaign (e.g., groundwater: (44 µgL^{-1} for Ba, 27 mgL^{-1} for Ca and 5.9 ‰ for δ^2H; soil water: 22310 µgL^{-1} for Ba, 23 mgL^{-1} for Ca). This resulted in high uncertainties in the calculated fractions (Table 4), and 10.4 ‰ for δ^2H; see Figure S2 for boxplots ofinhibits robust interpretation regarding the concentrations for the different water types). source areas.

4.4 Estimated solute concentrations based on conservative mixing of rainfall and baseflow

The concentrations estimated based on the assumption of conservative mixing between rainfall and baseflow (C_{es}, Eq. 3) differed from the measured stormflow concentrations (C_Q) for almost all solutes (Fig. 8). The measured concentrations for geogenic solutes (shown for calcium and sodium in Fig. 88a and b) were lower than the estimated concentrations. This could be due to mixing with a source with lower calcium or sodium concentrations (for instance soil water, or other contributions from the riparian areas; Table 2). The measured concentrations of sulfate (Fig. 8c) were lower than estimated based on conservative mixing as well, except for event II.I, III and IV. For potassium concentrations there was no clear pattern: the concentrations were underestimated and overestimated at both low and lower and higher discharges (Fig. 8d), which is probably due to the high discharge (Fig. 8).variation in soil water and groundwater potassium concentrations (Table 2). The measured concentrations of cobalt, copper, nickel and iron (solute groupsgroup A and C, see Fig. 6) were slightly lower than the estimated concentrations for low discharge, but (much) higher during high discharge (Fig. 8).8e-h). For copper and nickel this could be due to hillslope contributions, whereas for iron and cobalt it could be due to increased contributions from the riparian areas (see Table 2 and Table 3 for (ratios of) concentrations in different groundwater sources, as well as soil water and groundwater). There was no distinct threshold in the relation between C_Q/C_{es} and either discharge or the simulated fraction of the catchment that was connected to the stream (Fig. 8 and S5), C_Q/C_{es} rather changed gradually with increasing discharge and connected area.8 and S4).

5. Discussion

5.1 Small changes in streamflow composition compared to the spatial variability ~~in groundwater and soil water~~

Changes in solute concentrations in streamwater during rainfall events depend on ~~the~~ changes in the relative contributions of different sources to streamflow (e.g., event and pre-event water, or different pre-event water sources),~~ the differences in the concentrations of these sources,~~ as well as reactive transport processes. Our results show that the change in streamflow composition during the four rainfall events was ~~much~~ smaller than the spatial variability in groundwater and soil water composition. For instance, the ~~average~~ change in the concentration of barium and deuterium in streamflow for the ~~four events~~event with the largest changes was similar to the spatial variability in shallow groundwater and soil water measured after ~~events I and II (13.8~~that event (25 µgL^{-1} ~~Ba~~barium and ~~6.1~~5.0 ‰ change in ~~streamwater~~stream water, versus an interquartile range of 30 µgL^{-1} and 4.8 ‰ for shallow groundwater and 10.6 mgL^{-1} and 5.7 ‰ in soil water). This was also evident from the principal component analysis and mixing plots (Fig. 7). ~~It is to be expected that the change in streamwater composition is less than the variability between the end-members, but for~~For a viable hydrograph separation, the change in streamwater composition should be larger than the variability within the end-members (Hooper, 2001). ~~The change in streamwater composition during the four events presented in this study~~This was not the case for the Studibach catchment and thus the change in stream water composition was not large enough to distinguish contributions from ~~the~~ different (groundwater) sources, ~~although it is evident~~but the results did indicate that ~~pre-event water dominated streamflow.~~soil water fractions were considerable (about 0.3 to 0.4) for two out of the four events (Table 4).

We could show that the spatial variation within different source areas ~~was~~is large compared to the temporal variation~~ because~~, since we ~~collected~~had a large dataset of groundwater and soil water samples available. However, in other small catchment studies~~,~~ this comparison is often restricted, because of insufficient spatial sampling (Penna and van Meerveld, 2019). ~~Based on our experience for~~ Hence, in order to find out if the ~~Studibach, we see a clear need for further~~ spatial variation is also larger than the temporal variation in other locations (or if it is not), it is paramount to quantify the spatial variation by sampling ~~of~~ groundwater and soil water ~~in other~~ at multiple sites in more research areas. Then we will also know if the uncertainties (Table 4) are extreme or also typical for other catchments~~ to determine this spatial variability. ~~.

~~5.2 Which areas or sources contribute to stormflow?~~

The importance of soil water confirms earlier findings by Hagedorn et al.

~~For the events included in this study, the estimated area that was hydrologically connected to the stream was never smaller than a quarter of the catchment area, increased laterally upslope from the stream, and increased to a maximum of two thirds of the catchment area. The simulated connected area during a relatively small event (event I, total rainfall 17 mm) increased by a fifth of the catchment area, which implies that even small rainfall events can activate a sizable part of the catchment. The connectivity simulations for event II, however, suggest that during long duration low intensity rainfall events, the change in connectivity can be small. For this event, the relative contributions of soil water and rainfall to stormflow were much higher than for the other events (Table 4).~~

~~Using a combination of different tracers to identify the sources of streamflow can be helpful, because it enhances the likelihood that sources that contribute little to stormflow are identified (Barthold et al., 2017), and thereby reduces the risk of false conclusions about catchment functioning (Barthold et al., 2011). For instance, McCallum et al. (2012) used differential flow gauging and conservative (Cl) and non-conservative (Rn and EC) tracers to quantify the inflows and outflows of groundwater along three ~30 km long stream reaches in the Cockburn River, Logan River and Nambucca River catchments (> 400 km^2) in southeast Australia. They found that predictions made with flow data alone varied significantly from predictions that also included tracer data, and that the use of multiple tracers reduced the error in the calculation of the groundwater contributions.~~

Moreover, the discrepancy between the results of source-area analyses based on conservative and non-conservative tracers are hypothesized to indicate when other sources than baseflow and rainfall contribute to streamwater (Kirchner, 2003). We found that the event water fractions from two-component hydrograph separation (isotopes) and EMMA (multi-tracer) were comparable (Table 4). Similar to our results, Ladouche et al. (2001) found for the 0.8 km^2 Strengbach catchment in France that the hydrograph separation results based on $\delta^{18}O$ (f_{pe}: 10%) were relatively similar to the results of their mixing analyses (including DOC, Si, Ba, and U), and that a multi-tracer approach allowed them to distinguish between pre-event water contributions from the upper and lower part of the catchment. We found that concentrations of metals, such as iron or copper, were much higher than expected from mixing of rainfall and baseflow, whereas weathering-derived solutes, such as sodium or calcium, were lower than expected from mixing of rainfall and baseflow. We assume that the differences between measured and expected concentrations, particularly on the falling limb and at peak flow, are at least partly caused by contributions from groundwater sources or soil water (particularly for event II) that did not contribute to baseflow (see Table 3 for ratios of concentrations in different source waters). For instance, the differences for weathering-derived solutes could be due to contributions from soil water, which has lower concentrations of these solutes than groundwater. The concentrations of iron increased throughout the event until peak flow and were higher on the falling limb than on the rising limb. Since riparian groundwater has relatively high concentrations of iron (Table 2 and 3), contributions from riparian-like areas that did not contribute to baseflow (such as flatter areas away from the stream network) during rainfall events could explain this increase. Measured copper concentrations were much higher than expected for events III and IV, but lower than expected for most samples of events I and II. Because copper concentrations are relatively high for hillslope groundwater and low in soil water (Table 2 and 3; Kiewiet et al., 2019), this could be an indication that the hillslopes did not actively contribute to streamflow during event I and II, and were only activated after peak flow for events III and IV (see wide hysteresis for event I in Fig. 5, top row). However, the copper concentrations should then also not have increased compared to baseflow during event II, which was not the case (maximum R_{Cu} during event II: 1.7 vs 1.0, 1.0 and 1.4 during event I, III and IV, respectively). The potassium concentrations were too variable to aid further interpretation, which is probably due to the high variation in potassium concentrations in soil water and groundwater (Table 2).

The contribution from soil water was considerable (f_{SW}: 0.27) for only one of the four events (event II, Table 4). This was a long, low intensity event, occurring on a relatively 'dry' catchment (baseflow event I and II: 0.2 mm h^{-1} vs. 0.7 mm h^{-1} for event III and IV). Hagedorn et al. (2000), who analysed three rainfall events (7 mm, 8 mm and 30 mm rainfall) in the neighbouring Erlenbach catchment and showed a large contribution of soil water to streamflow. Their. The mixing diagrams using chloride and calcium in their study indicate that the average contribution of the top soil to streamflow was larger than 50%. However, chloride and calcium concentrations vary considerably in both soil and groundwater (average coefficient of variation: 0.86 and 1.0 for eight soil water (n=6 to 18) and 1.0 and 0.3 for nine groundwater (n=34 to 47) snapshot campaigns for chloride and calcium respectively). Furthermore, the concentration of bivalent cations, like calcium, in rainwater can increase during transportrapidly in throughfall through the canopy leaching (Lindberg et al., 1986). Moreover, van Meerveld et al. (2018) showedfound that calcium concentrations in overland flow from small landslide areas in the Studibach were much higher than for other solutes, indicating rapid dissolution as well. The much lower soil water contributions found for this study compared to Hagedorn et al. (2000) may thus be partly caused by the choice of the tracers. Understanding the role of soil water for runoff generation processes is challenging because of the spatial variation in its amount (e.g., McMillan and Srinivasan, 2015), the horizontal and vertical spatial variation in soil water chemistry (Gotteselig et al., 2016), and the importance of preferential flow (e.g., Wiekenkamp et al., 2015). Antecedent soil moisture conditions also affect runoff amounts and stream chemistry (Zehe et al., 2010; Uber et al., 2018; Knapp et al., 2020), as well as hillslope-stream connectivity (Penna et al., 2011). Further investigation of the response of soil water, the distribution of soil water chemistry and the interaction between soil water and groundwater during rainfall events is thus important if we want to understand the influence of soil water on hydrologic connectivity and when and where soil water contributes to streamflow..

5.2 Which areas contribute to stormflow?

The presence of different ‘old’ water stores in the catchment, which are mobilized in different proportions at high and low flows, can cause changes in stream water composition during events (Kirchner, 2003). To illustrate this, we tested if simple mixing of baseflow and rainfall could explain the solute concentrations in stream water during events. We found that the measured and expected concentrations differed for most solutes (Fig. 8). Concentrations of metals, such as iron or copper, were much higher than expected from mixing of rainfall and baseflow, whereas weathering-derived solutes, such as sodium or calcium, were lower than expected. We interpret the differences between the measured and expected concentrations, particularly on the falling limb and at peak flow, to be at least partly caused by contributions from soil water or groundwater sources that did not contribute to baseflow (see Table 3 for ratios of concentrations in different source waters). For instance, the differences for weathering-derived solutes could be due to contributions from soil water, which has lower concentrations of these solutes than groundwater. The concentrations of iron increased throughout the event until peakflow and were higher on the falling limb than on the rising limb. Since riparian groundwater has relatively high concentrations of iron (Table 2 and 3), elevated contributions from riparian areas throughout the rainfall events could explain this increase. Measured copper concentrations were much higher than expected for event III and IV, but lower than expected for event I and II. Because copper concentrations are relatively high on the hillslopes and low in soil water (Table 2 and 3; Kiewiet et al., 2019), this could be an indication that the hillslopes did not actively contribute to streamflow during these events, and were only activated after peak flow (see wide hysteresis for event I in Fig. 5, top row). However, then the copper concentrations should also not have increased relative to baseflow during event II, which was not strictly the case (maximum R_{Cu} during event II: 1.7 vs 1.0, 1.0 and 1.4 during event I, III and IV, respectively). In any case, the solute concentrations could not be explained as the simple mixture of rainfall and baseflow for any of the events, but the differences between the expected and measured concentrations can at least partly be explained by contributions from other (groundwater) source areas.

For the events included in this study, the

The typically moderate event-water fractions could indicate that overland flow is of minor importance for streamflow in the Studibach. However, overland flow does occur in the Studibach (van Meerveld et al., 2018). Saturation overland flow has been observed during sprinkling events for other sites on gleysols in Switzerland as well (Feyen et al., 1996; Weiler et al., 1999; Badoux et al., 2006). Given the low event-water fractions, we suspect that the overland flow mixes with pre-event soil water on its way to the stream (Kienzler and Naef, 2008; Elsenbeer and Vertessy, 2000), or originates from exfiltrating soil water or groundwater and thus does not have the same composition as rainwater (Barthold et al., 2017). Alternatively, overland flow may infiltrate in unsaturated soils before reaching the stream, and thus not influence the streamwater composition.

5.3 Hydrologic connectivity and streamwater chemistry

The simulations of the active and connected area suggest that area estimated to be hydrologically connected was never smaller than a quarter of the entire catchment area, increased laterally upslope from the stream, and reached a maximum of 0.68 of the entire catchment area. The simulated connected area during a relatively small event (event I, total rainfall 17 mm) increased by 0.20, which implies that little precipitation can activate large parts of the catchment. The simulations of the active and connected stream network confirm that the near-stream areas are most often connected and respond first to rainfall, highlightingwhich shows their importance for the rapid generation of streamflow. The model results also showed that some areas remain disconnected from the stream (Fig. 4). Nippgen et al. (2015) found very similar connectivity patterns for a subcatchment of the Tenderfoot Creek Experimental Forest (5.55 km^2) in central Montana, USA. They simulated the connected area over a two-year period and found that it expanded from areas parallel and close to the stream during low-flow conditions, to the hillslopes during high-flow conditions, and that 10% of the catchment was never connected to the stream.

The change in streamwater chemistry (Fig. 4). The difference between the expected and measured concentrations (Fig. 8) also suggests that the quick increase in connected area increased rapidly becauseis important: even for small increases in discharge, stormflow could not be described as a mixture of rainfall and baseflow. However, there was no clear relation between the extent of the hydrologically connected area and the discrepancy between the relative changes in the concentrations of conservative and non-conservative solutes (Fig. S5). Other studies that used streamwater chemistry to investigate hydrological connectivity focused on one tracer that was clearly different for different source areas (e.g., Soulsby et al., 2007; Ocampo et al., 2006). These studies illustrated that for some catchments the changes in streamwater chemistry reflect changes in hydrological connectivity. However, other studies showed that the interpretation of stream-based measurements may not always be straightforward because the changes in streamwater chemistry can be obscured by dampening and mixing processes (Tezlaff et al., 2014), or because a tracerHowever, the connectivity simulations for event II suggest that connectivity can change little during long, low-intensity rainfall events. This might only reflect connectivity to a specific part of the catchment, rather catchment-wide connectivity (e.g., areas with high DOC concentrations for Pacific et al., 2010). For instance, Pacific et al. (2010) compared changes in streamwater DOC concentrations with estimates of upslope-riparian-stream (URS) connectivity (methods cf. Jenceo et al., 2009) in the Tenderfoot Creek catchment. They found a negative (though insignificant) relation between stream DOC export and URS-connectivity, and showed that URS-connectivity is particularly important to predict DOC export when areas with high DOC concentrations are connected to the stream. Multiple studies in the Girnock catchment in Scotland used streamwater Gran alkalinity and isotopic composition to investigate hydrologic connectivity (Soulsby et al., 2007; Tezlaff et al., 2014). Birkel et al., (2010), furthermore, explored the catchment's functioning with a spatially and temporally dynamic saturation model. These studies found that contributions from the upper soil layers and upslope areas dominatedbe reflected in the higher soil water and rainfall fractions in stormflow for event II, whereas typically groundwater dominates streamflow in this catchment.

Given the typically moderate event-water fractions, we expect that surface runoff is likely to be of minor importance for streamflow, although surface runoff does occur in the Studibach (van Meerveld et al., 2018). at higher flows and that there was a soil moisture threshold for the contribution of these sources (Birkel et al., 2010). Furthermore, Tezlaff et al. (2014) showed that the dynamic behaviour of the isotopic composition of streamwater was in the range of the composition of soil water from the riparian peat soils at 10 and 30 cm deep , and only deviated from this range during some larger events. They concluded from these results that precipitation inputs drive the dynamics of streamflow and streamwater isotopic composition but that the streamflow responses are dampened because the water travels through different hydropedological units.

Alternatively, it may have infiltrated through macropores or unsaturated soils before reaching the stream. This corresponds to the event-water fractions based on the two-component hydrograph separation (event-average event water fraction: 0.03±19 to 0.24±0.31), but less with the EMMA results (range: 0.25±1.24 to 0.47±0.40, Table 3), and indicates that contributions from other sources than rainfall are likely important.

Despite substantiallarge changes in the hydrologically connected area and the large spatial variability in groundwater composition, we did not observe a distinct threshold in the relation between the deviation of stream chemistry from simple conservative mixing of rainfall and baseflow and either streamflow or the connected area. The. This gradual change in streamwater chemistry might reflectbe caused by the (relatively) gradual increase in the connected area with increasing discharge for all of the studied events, except event I, for which the connectivity increased abruptly after peak discharge (top row in Fig. ~~5).~~ 5). Alternatively, the change in stormflow composition could be the result of the mixing of a large number of source areas. Abbott et al. (2018) showed that ~~changes~~the change in ~~streamwater~~streamflow composition with increasing discharge and connectivity ~~are~~is less pronounced for catchments with a myriad of source areas than for catchments with fewer different landscape elements. The Studibach is characterized by many small landscape elements, particularly steep hillslopes and ~~flatter~~flat, wet areas, which formed due to landslides and soil creep~~,~~ and ~~which induce~~induced small-scale differences in ~~drainage and thus~~ soil and vegetation development. Hence, activation of different landscape elements might occur ~~gradually and~~semi-simultaneously at ~~many~~ different places across the catchment (i.e., the connected area extends from flat locations to the hillslopes at many different ~~locations~~transects), but the outflows of these elements ~~all have a slightly different chemical composition.~~mix on its way down to the outlet. From this perspective, it is ~~perhaps~~ not surprising that solute concentrations in stormflow changed little compared to the spatial variability in the end-member composition ~~because streamflow~~. Streamflow is a mixture of ~~the many~~ different water sources in a heterogeneous catchment.

~~Alternatively, the simulations of the active and connected areas might overestimate the change in the source areas compared to reality. Although most flow occurs in the upper, more permeable layer of the soil, seepage to deeper soil layers (Feyen et al., 1999), or to the bedrock in areas where there is no continuous groundwater table in the gleysol, may have decreased the downslope travel distance (cf. Jackson et al., 2014). We did not consider a limitation of the downslope travel distance due to bedrock infiltration because the occurrence of a permanent water table in a large part of the catchment implies that percolation to the bedrock is very slow. However, bedrock infiltration might occur at some locations (e.g., the more densely rooted forested sections on steeper better-drained soils), and might decrease the lateral distance that a water parcel can travel. Additionally, we did not consider an offset in the timing of the simulated connectivity and response in streamwater chemistry due to the travel time to the stream or mixing of hillslope and riparian groundwater in the riparian zone. Chanat and Hornberger (2003) showed with a virtual experiment for a 10 km^2 hypothetical catchment that the change in the chemical signature of the streamwater can be delayed relative to the change in discharge, and that this delay was larger when the near-stream reservoir (i.e., riparian zone) was larger. Their findings are thus especially important to consider for 'wet' catchments that have a large near-stream reservoir, or for which the near-stream reservoir expands quickly. Furthermore, the stormflow composition is the result of mixing of contributions from different source areas. Subsurface mixing can result in temporally variable end-member compositions. Frameworks to handle time-variable end-member compositions exist (Harris et al., 1995), but there are obvious challenges, such as measuring these time variable compositions. Furthermore, mixing of different water sources will dampen the tracer signal (Abbott et al., 2018; Tezlaff et al., 2014) or may even chemically 'reset' the hillslope signal as it mixes with riparian groundwater (Tezlaff et al., 2014; Lidman et al., 2017).~~

6. Conclusions

The results of this study ~~show~~showed that the spatial variability in soil water and groundwater composition across ~~the~~a small pre-alpine headwater ~~study~~ catchment ~~was large. Hydrograph separation and EMMA indicated that pre-event groundwater~~is larger than the temporal variation in stream water during events. This resulted in very large uncertainties in the estimated source water fractions. Groundwater was the dominant source of streamflow~~, and that soil water contributions were minimal~~ for three of the four events. ~~For most solutes, the streamwater~~Soil water contributions were very small for two events. The stream water concentrations could not be explained by conservative mixing of baseflow and rainfall~~.~~ for most solutes. The differences were largest at high discharge~~. This suggests~~, indicating that this ~~deviation~~ may ~~indicate~~be caused by the ~~contribution~~contributions from ~~new contributing~~other sources due to the expansion of the connected area. ~~Concentrations of weathering-derived solutes decreased more than expected, which might be due to the contributions of soil water. In contrast, concentrations of iron and copper increased more than expected, which might be due to contributions from riparian-like areas~~

~~and hillslopes, respectively. Thus, the differences between the expected and measured concentrations could be partly explained by contributions from other source areas.~~ However, there was no threshold in the relation between ~~streamflow and~~ the deviations of the ~~measured~~ concentrations ~~and~~from the expected concentrations based on ~~conservative~~ mixing, suggesting that there was no sudden activation of source areas~~. The lack of a threshold-relation between the deviations in the solute concentrations and streamflow made it more difficult to infer changes in hydrological connectivity from the streamwater solute concentrations. Overall this work shows that inferring hydrological connectivity from solute concentrations is not straightforward, especially if we consider the large variability of the tracer concentrations in the different water sources. The~~ to cause the observed changes in concentrations. Instead, the gradual changes in ~~streamwater chemistry during events~~ solute concentrations are likely the result of increases in the contributions from many (small) landscape elements in the catchment and ~~reflect~~ the gradual increase in connectivity during events. The modelled hydrologically connected area and changes in solute concentrations both suggest that source areas change during events. This highlights the importance of characterizing the composition of different source areas, and the spatial variability within these areas when using stream-based measurements to investigate hydrologic connectivity.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

LK and IVM conceptualized the study. LK collected and analysed the data, and prepared the ~~first draft of the~~ manuscript. IVM, JS and MS provided recommendations for the data analysis, participated in discussions about the results, and ~~edited and commented on~~revised the manuscript.

Competing interests

The authors declare that they have no competing interests.

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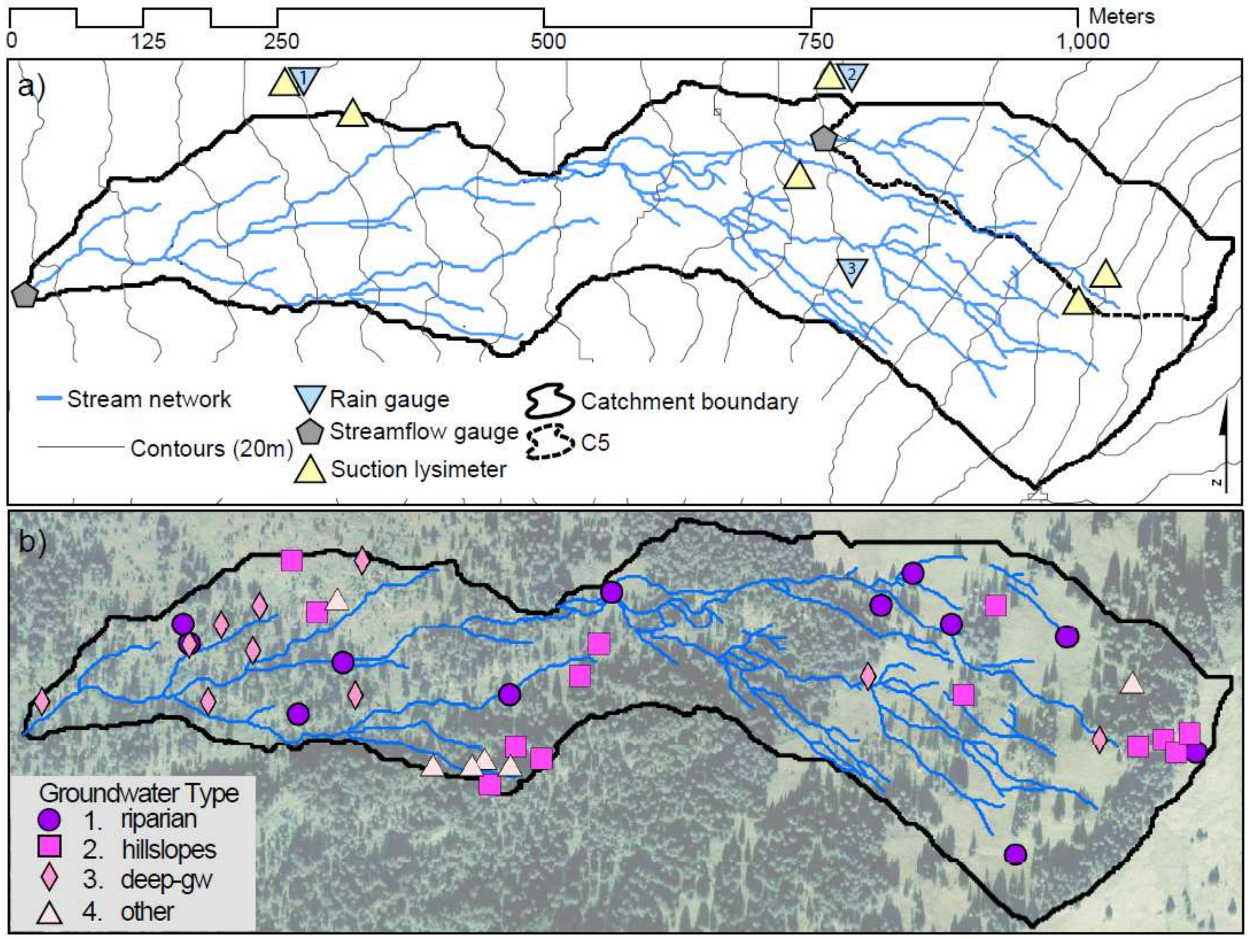
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3. deep-gw
4. other

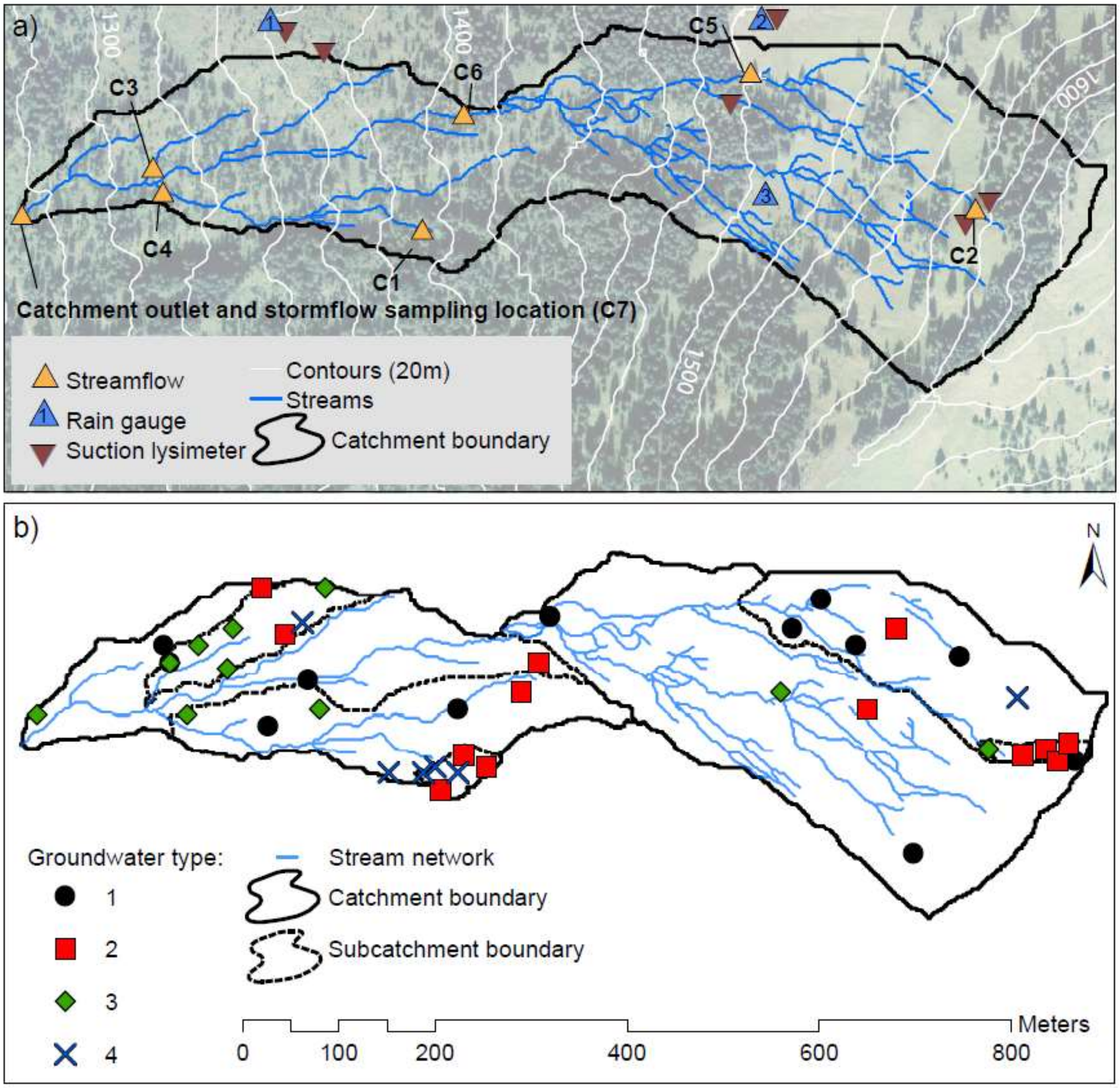


Figure 1. Maps of the Studibach catchment with a) the stream network (blue lines), stream gauges (~~grey pentagons~~orange triangles), rain gauges (blue ~~reversed~~ triangles, 1 – 3) and suction lysimeters (~~yellow~~brown reversed triangles), 20 m contour lines (~~grey~~white) and the ~~boundary of the~~ catchment boundary (black~~) and C5~~); b) sub-catchment boundaries (dashed lines) and ~~b)~~ location of the wells, ~~colour~~color coded by groundwater type 1. riparian wells; 2. hillslope wells; 3. 'deep' groundwater wells; 4. wells with high magnesium and sulfate ~~concentrations (~~concentration based on Kiewiet et al~~.,~~. (2019).

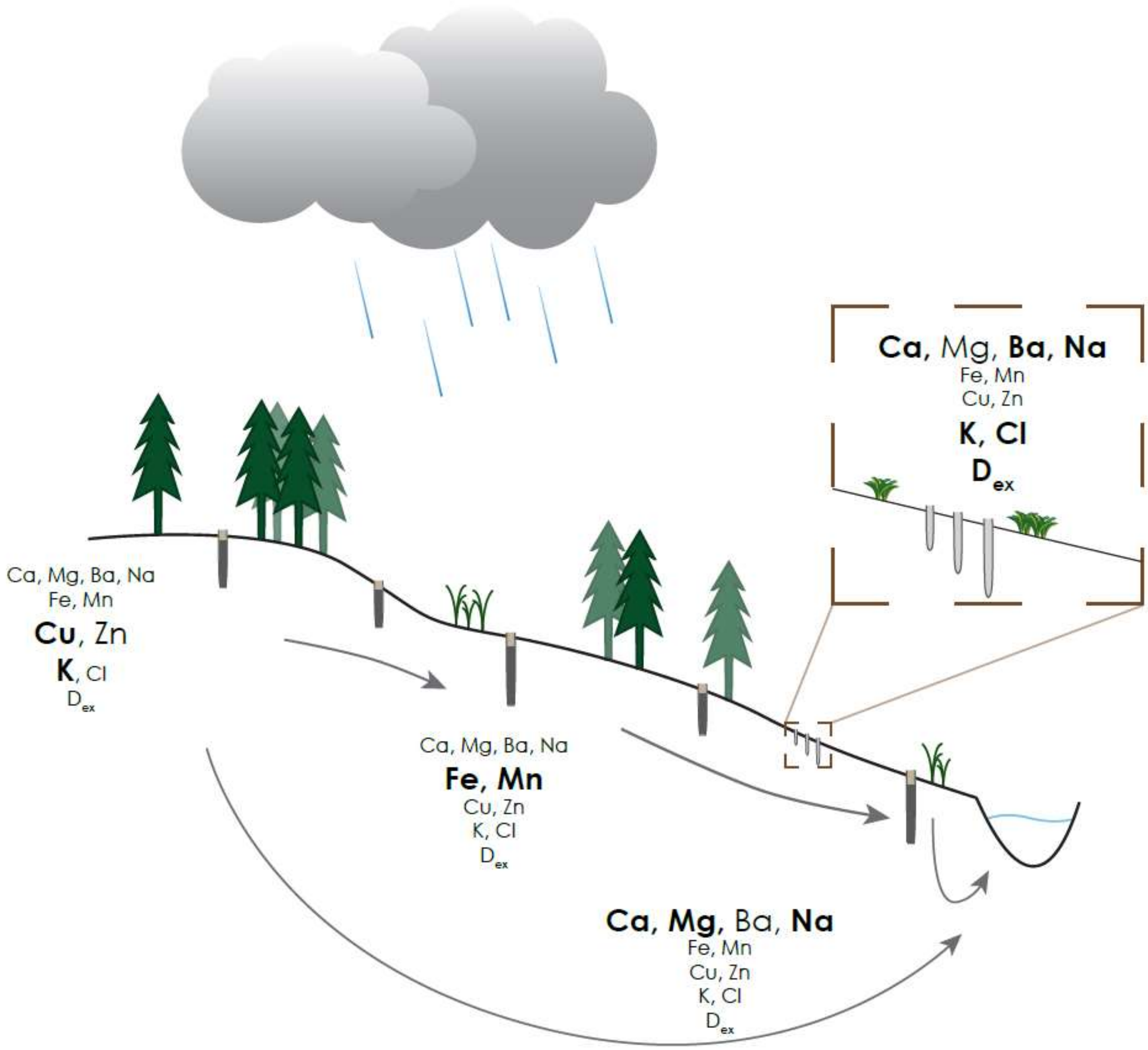
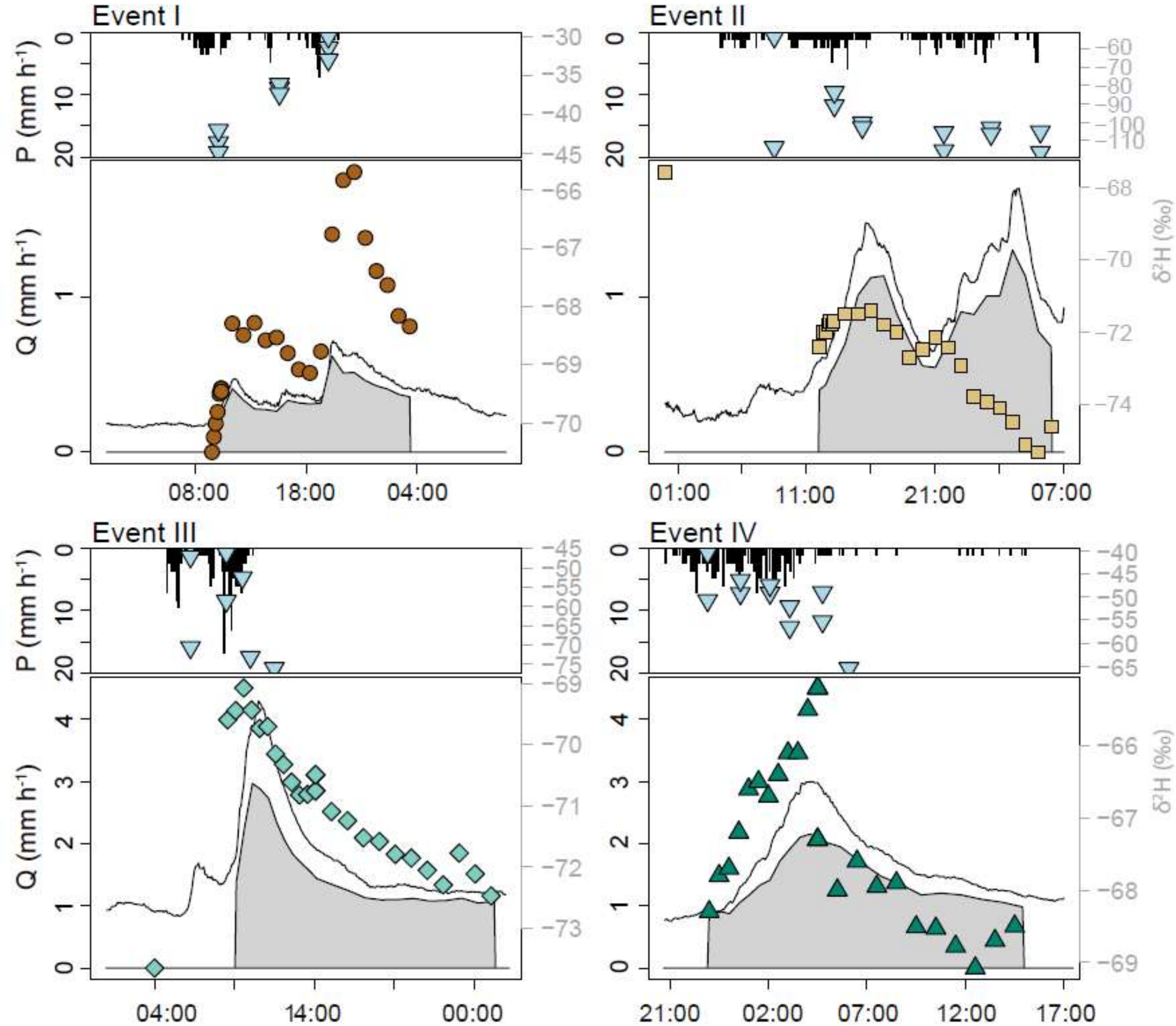


Figure 2. Illustration of a hillslope cross-section with different (ground)water compartments (based on Kiewiet et al., 2019 and Table 2), showing the tracers used in combination with δ^2H and $\delta^{18}O$ to characterize the different source areas. For most elements, the concentrations were low in rainfall compared to the concentrations in the other water compartments. High potassium, barium and chloride concentrations and high deuterium excess (D_{ex}) are indicative of soil water. For shallow groundwater, the concentrations of copper and potassium were higher at (forested) ridge locations, whereas for sites with water tables that are persistently close to the surface, the concentrations of iron and manganese were higher. We assume that higher concentrations of geogenic solutes (calcium, magnesium and sodium) indicate longer subsurface residence times. The isotopic composition for the different water compartments depends on the composition of recent and current precipitation.


Event I
Event II
Event III
Event IV
P (mm h-1)
Q (mm h-1)
δ2H (‰)
08:00
18:00
04:00
01:00
11:00
21:00
07:00
04:00
14:00
00:00
21:00
02:00
07:00
12:00
17:00

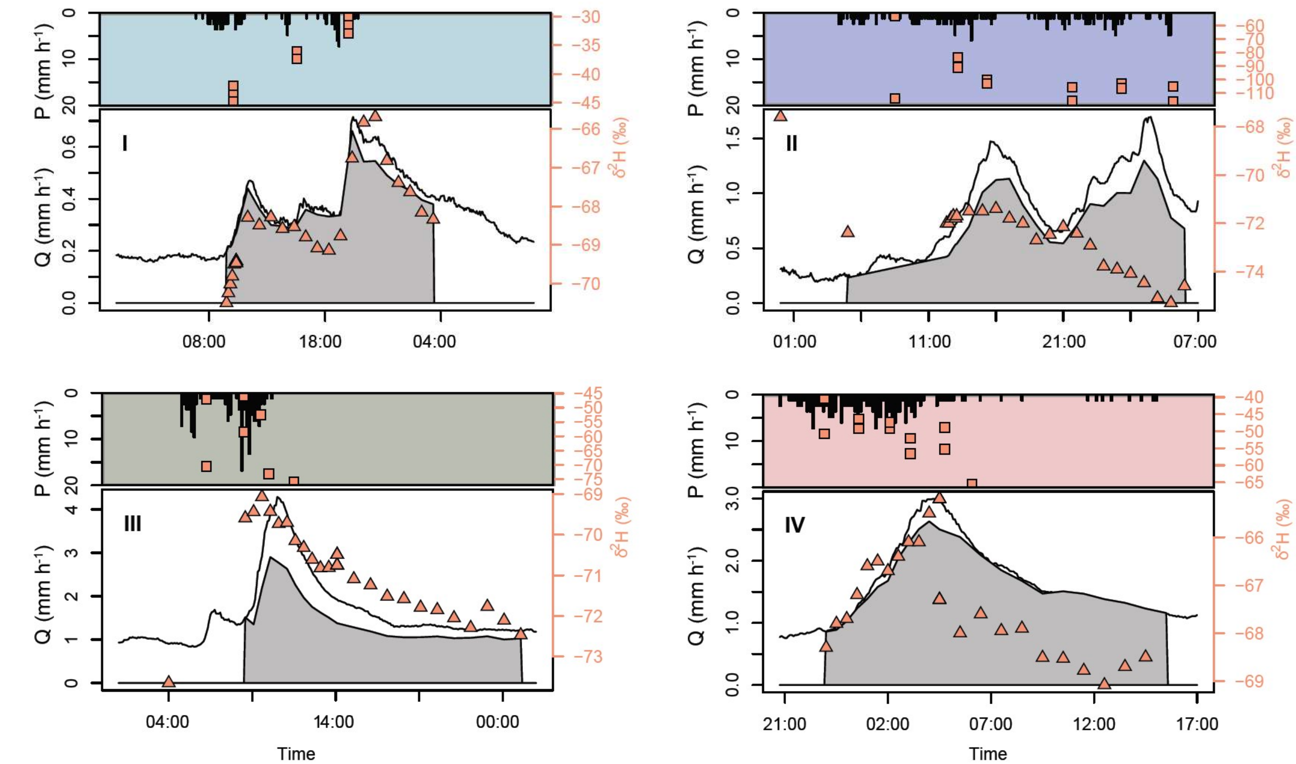


Figure 3. Hydrographs and hyetographs for the four ~~studied~~ events (I – IV). For each event, the upper panel shows the 10-min rainfall intensity (mm h^{-1}, bar graph) and the isotopic composition of the rainfall (δ^2H in ‰, ~~light blue reversed triangles~~orange squares), while the lower panel shows the discharge at the catchment outlet (mm h^{-1}, solid line), the isotopic composition of ~~streamwater~~stream water (δ^2H in ‰, ~~brown dots, light brown squares, turquoise diamonds and green~~orange triangles ~~for event I-IV, respectively~~), and the pre-event water fraction of streamflow based on two-component hydrograph separation using δ^2H (grey polygon) as a tracer.

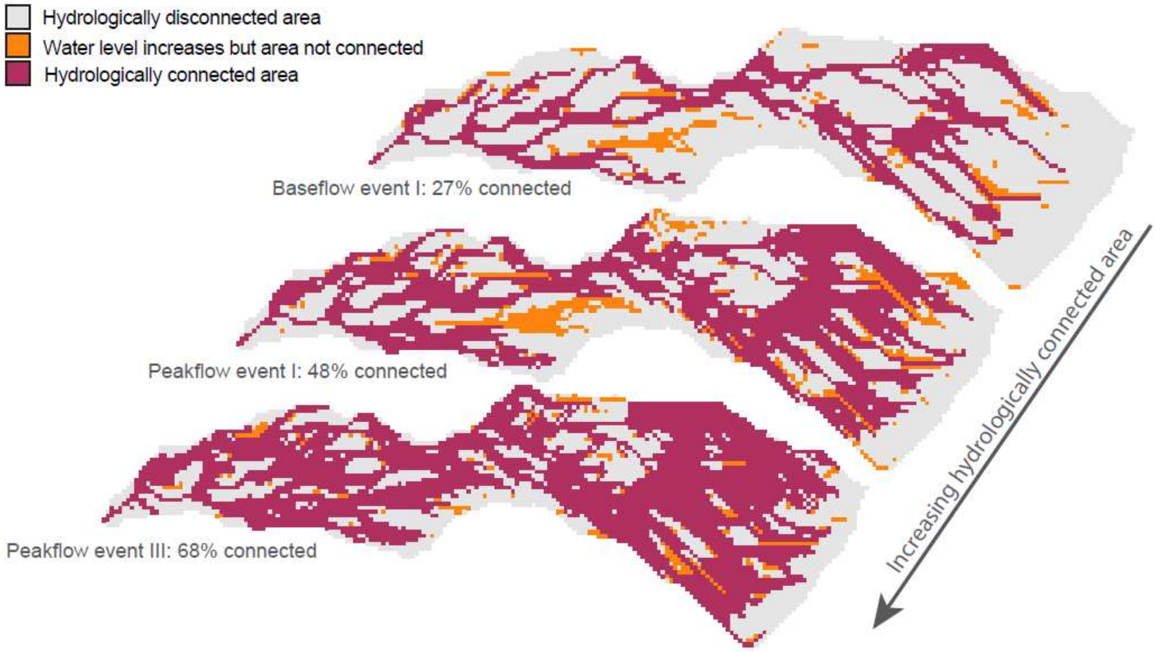
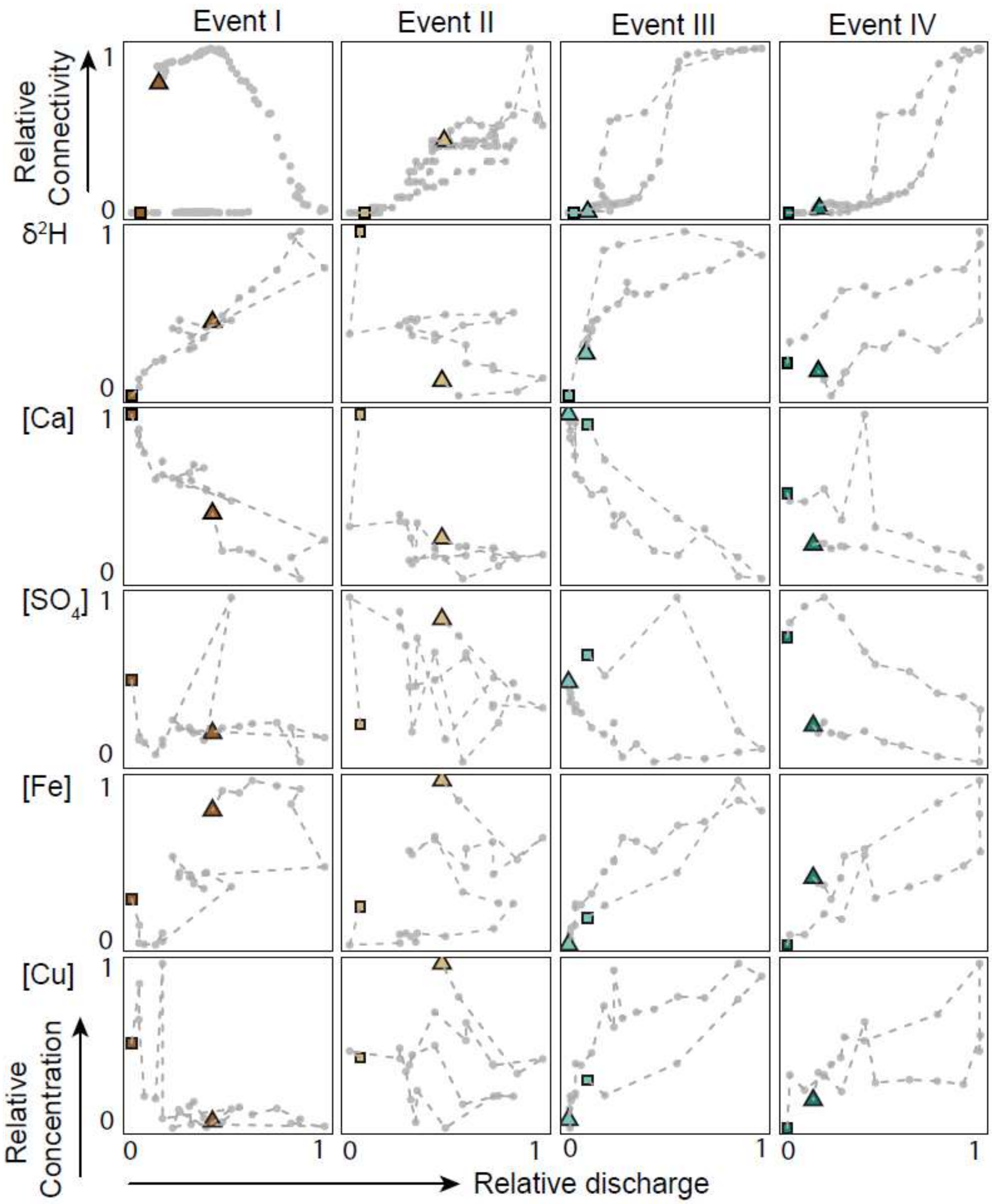


Figure 4. The simulated spatial pattern of the hydrologically connected area for three different flow conditions: from relatively low flow (baseflow prior to event I; top), to intermediate flow conditions (~~peak flow~~peakflow during event I; middle), to the period of highest discharge for the studied events (~~peak flow~~peakflow during event III; bottom). Grey indicates the hydrologically disconnected areas (water level more than 30 cm from the soil surface), red indicates the hydrologically connected area (i.e., water level within 30 cm from the soil surface and connected to the stream via other active areas), and orange indicates the active but disconnected area (i.e., the water level increased into the upper 30 cm of the soil but is not connected to the stream ~~network~~ by other active areas). The connected area was simulated based on the measured groundwater levels and a data-driven model that uses surface topography to estimate the water level for unmonitored grid cells~~ (cf.~~, following the methodology of Rinderer et al~~.,~~. (2019).


Event I
Event II
Event III
Event IV
Relative Connectivity
δ²H
[Ca]
[SO4]
[Fe]
[Cu]
Relative Concentration
Relative discharge
0
1

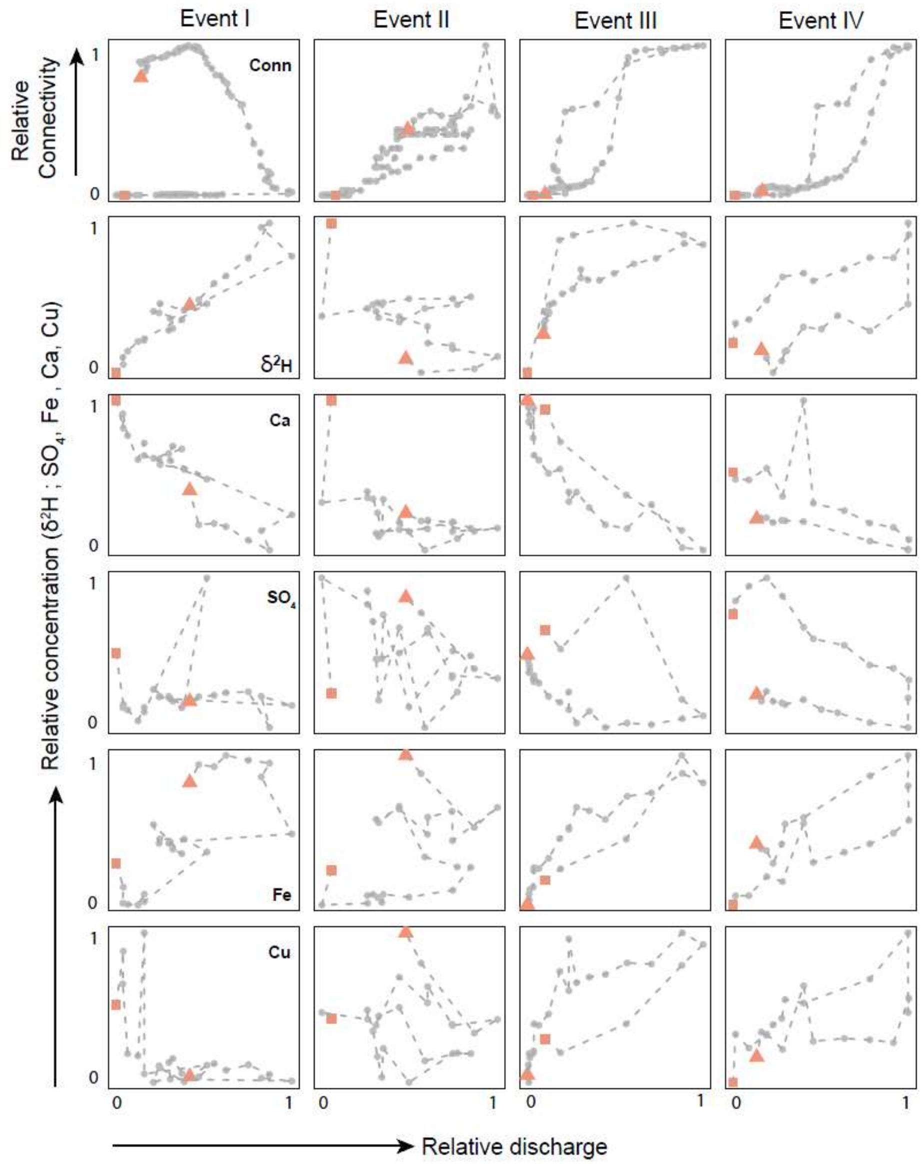
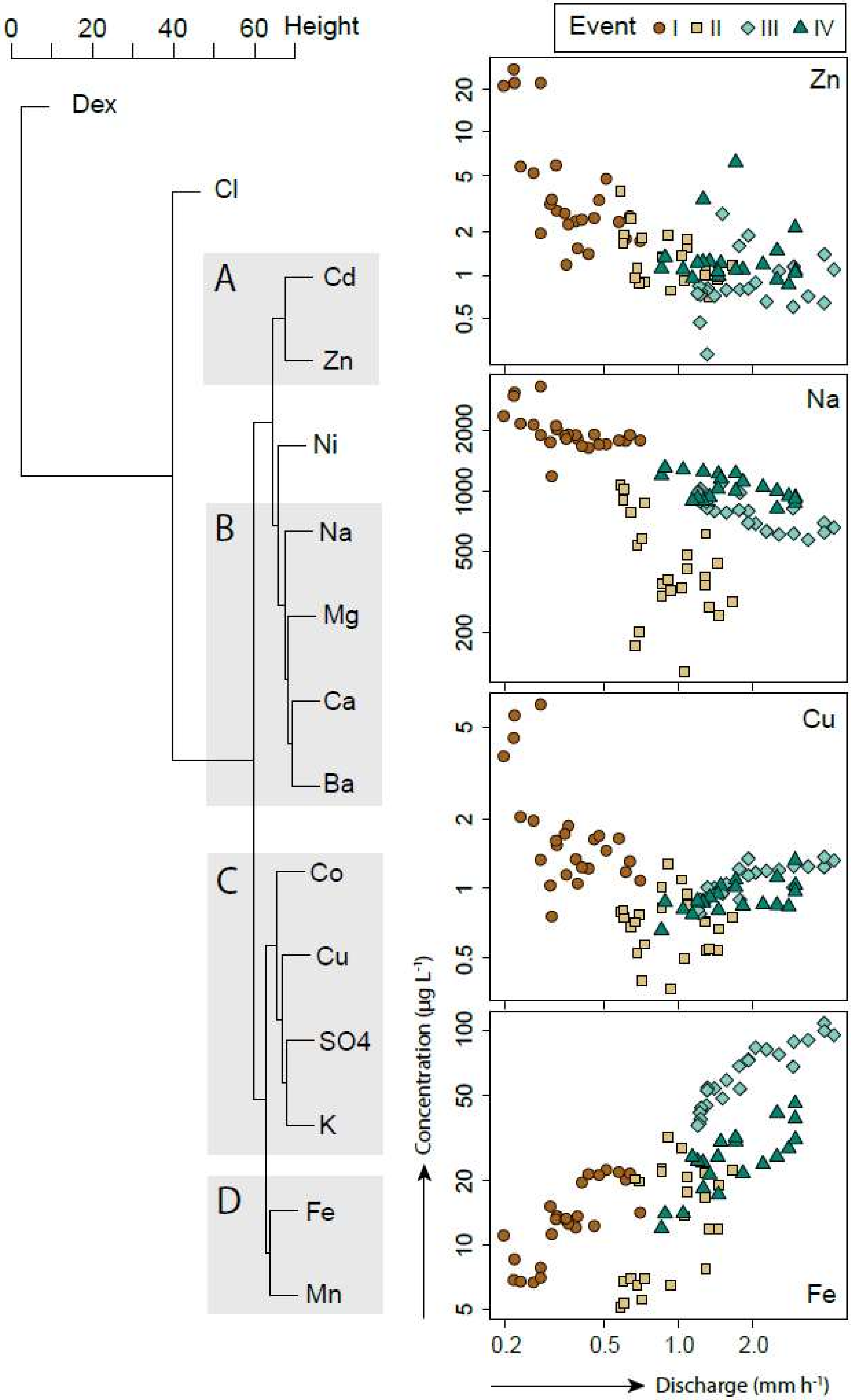


Figure 5. ~~Relationship~~Relation between the fraction of the catchment that was connected (~~relative connectivity~~Conn) and discharge (top row~~),~~) and concentration-discharge relationships for δ^2H, calcium, sulfate, iron and copper (rows 2-6) from the start (orange square) until the end (orange triangle) of the event for events I-IV (columns). Individual samples are marked with a grey dot and connected with a dashed line~~, the first sample of the event is indicated by a square, and the last sample by a triangle.~~. All data are normalized between 0 (minimum measured value for the event) and 1 (maximum measured value for the event) ~~for~~to better ~~visualization of~~visualize the hysteretic relation.



0
20
40
60
Height
Dex
Cl
A
Cd
Zn
Ni
B
Na
Mg
Ca
Ba
C
Co
Cu
SO4
K
D
Fe
Mn
Event
I
II
III
IV
Zn
Na
Cu
Fe
Concentration (µg L⁻¹)
Discharge (mm h⁻¹)
0.2
0.5
1.0
2.0

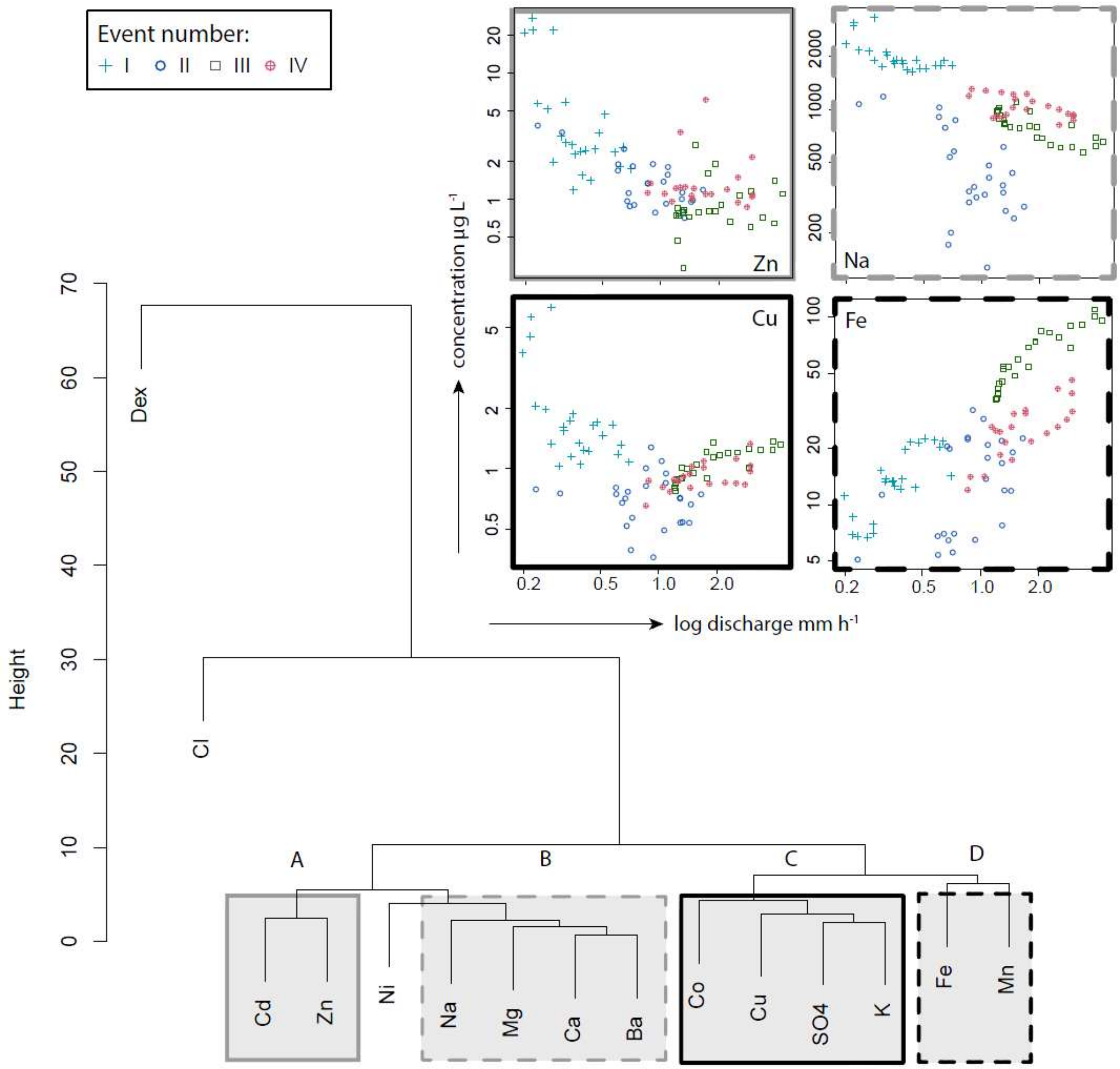
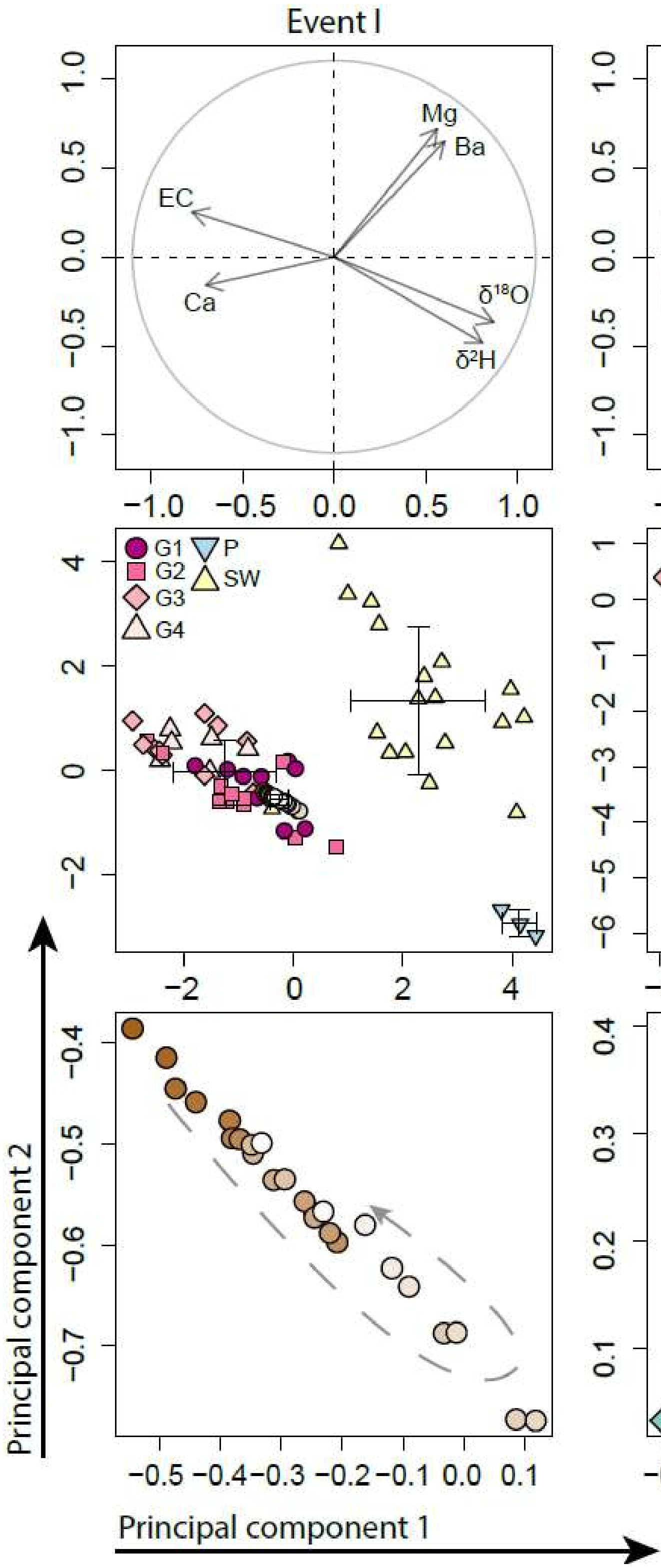


Figure 6. Bottom: Dendrogram for the hierarchical clustering of solutes and D_{ex} based on the magnitude and timing of changes in streamflow concentrations compared to the baseflow concentration (R_x; Eq. 2) during the four events ~~(I-IV), and~~, with different groups (A-D) marked in grey boxes, and top: concentration-discharge relationships for one solute from each ~~group (A-D).~~ of the four groups (different symbols indicate the different events).



Event I
Event III
Mg
Ba
EC
Ca
δ18O
δ2H
G1
G2
G3
G4
P
SW
Principal component 2
Principal component 1

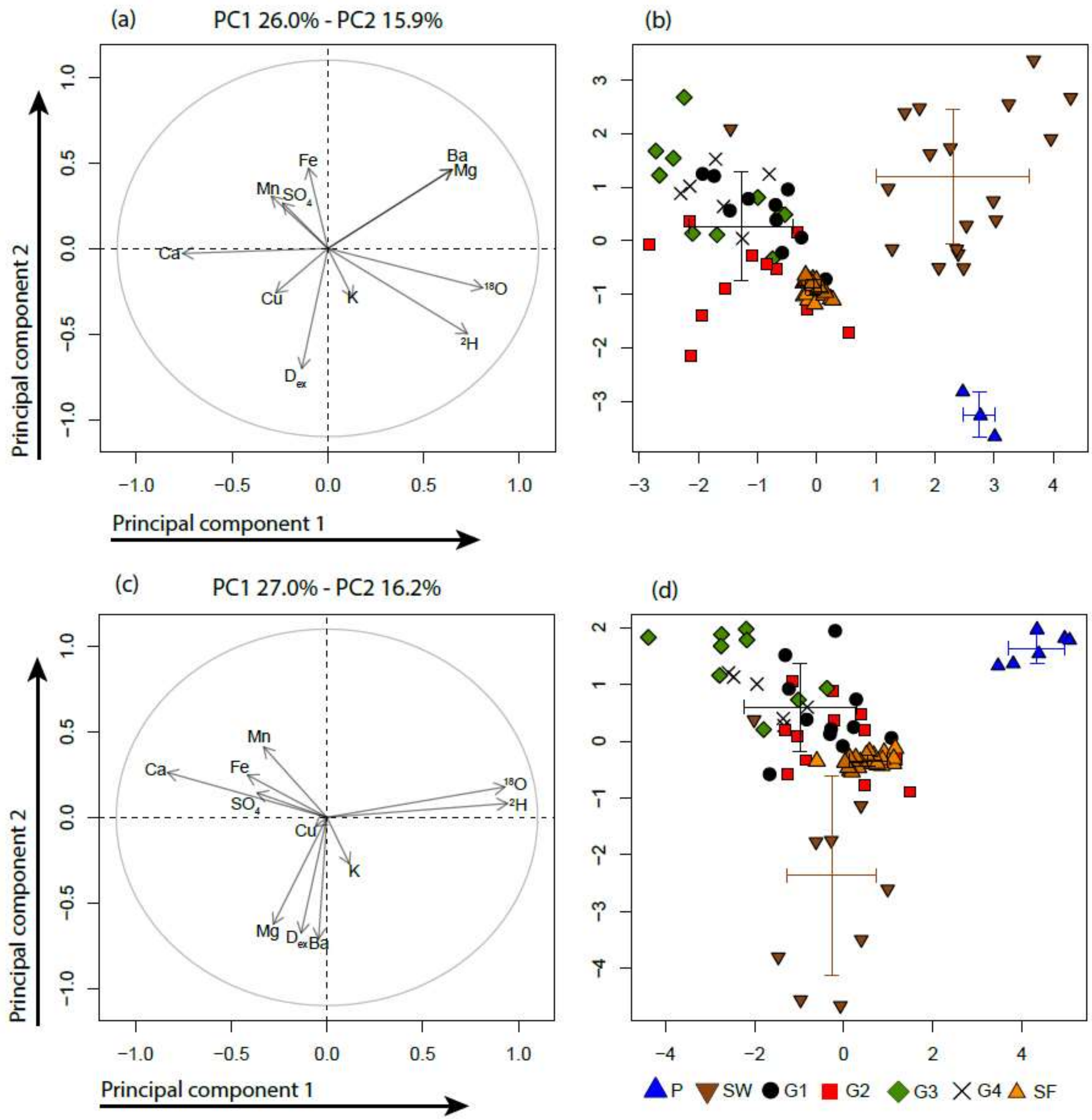
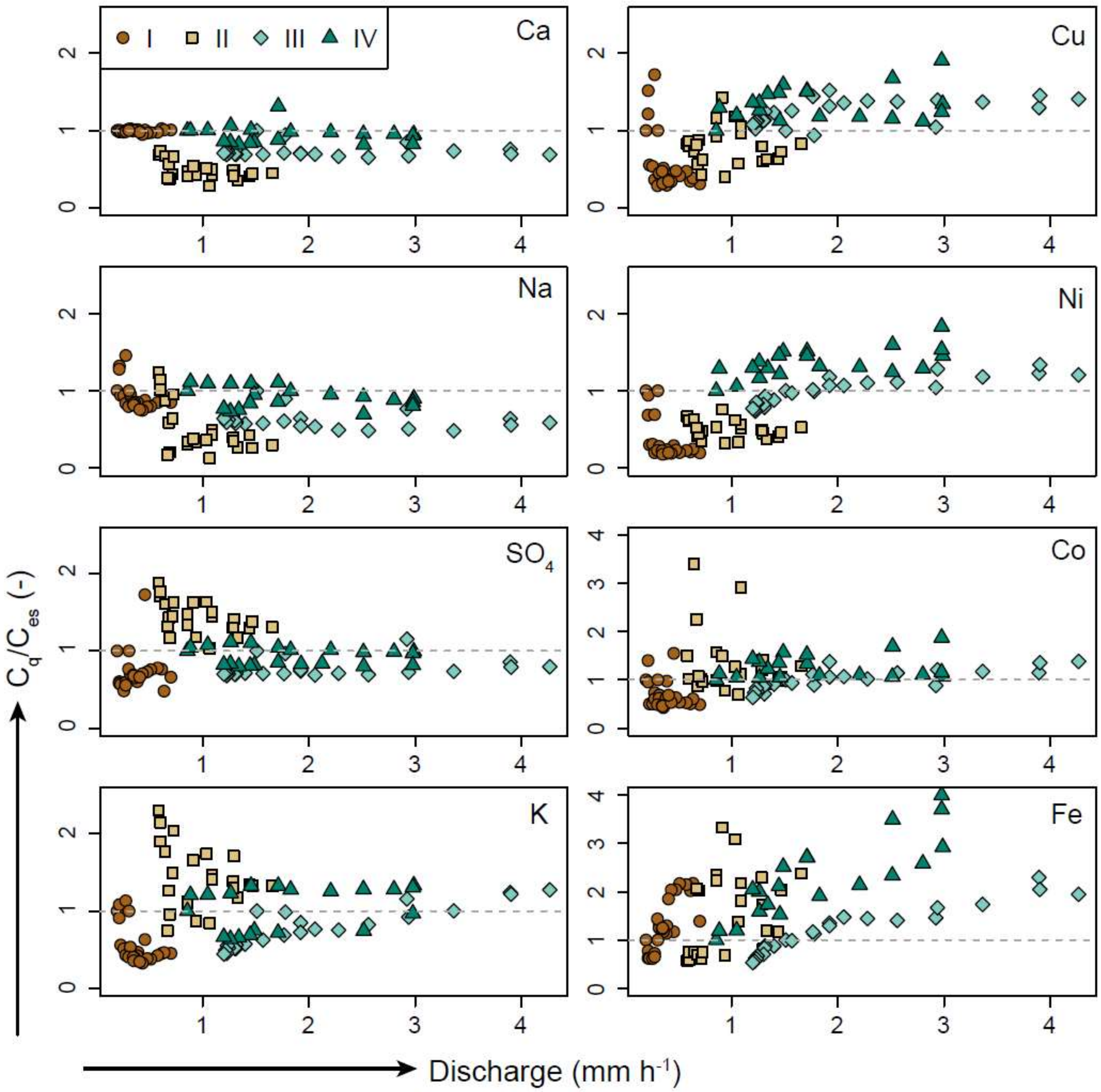


Figure 7. PCA results and mixing diagrams for ~~events~~event I (a and b) and event III (c and d). Event I is representative of a small event~~) and III (~~, whereas event III is representative of an intermediately sized event~~)~~. In the biplots (~~top row~~a and c), the length of the arrow represents the explanatory power. The mixing diagrams based on the first two ~~principal~~principle components (~~middle row~~b and d) show the individual rainfall (~~light~~ blue triangles), soil water (brown reversed triangles), ~~soil water (yellow triangles), and~~ and groundwater samples (~~purple~~black circles, ~~pink~~red squares, ~~light pink~~green diamonds and ~~rose triangles~~black crosses, representing groundwater types 1-4 based on Kiewiet et al., 2019), the streamflow ~~(Q)~~ samples~~,~~ (SF, orange triangles), as well as the average and standard deviation for each component (error bars). ~~The third row shows a zoom-in of the streamflow samples and highlights the evolution of the streamwater composition (colours fade to white towards the end of the event); the general direction of change is indicated with a grey arrow and dashed lines.~~ The biplots and mixing plots for the events II and IV are ~~shown~~given in the supplementary material ~~S4.~~S3.


I
II
III
IV
Ca
Cu
Na
Ni
SO4
Co
K
Fe
Cq/Ces (-)
Discharge (mm h-1)

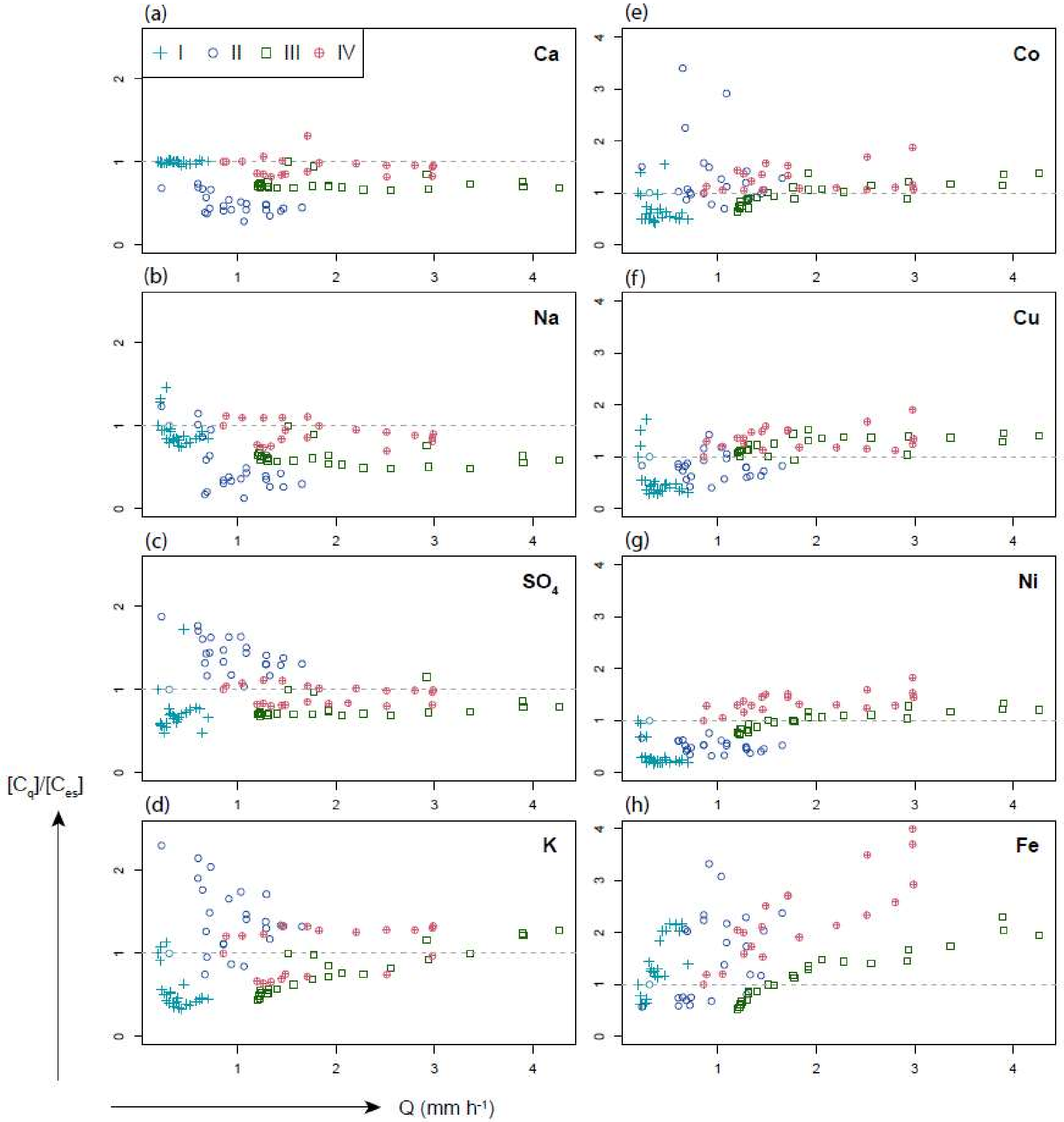


Figure 8. The ratio of the measured (C_Q) and estimated stormflow concentrations (C_{es}; Eq. 3) for calcium, sodium, sulfate, potassium, cobalt, copper, nickel and iron as a function of the specific discharge (Q) at the catchment outlet. The dashed grey line indicates where C_Q and C_{es} are equal; the different symbols reflect the different events (I-IV). Note the difference in scale for ~~cobalt~~the left and ~~iron.~~right column. For the relation with the ~~simulated~~ fraction of the catchment that was connected to the stream see ~~Figure S5~~S4.

Table 1. Overview of the four events analysed in this study: event duration (D, h), rainfall amount (P, mm), average and maximum 10-min rainfall intensity (I_p and $I_{p\text{-max}}$, mm h^{-1}), the maximum changerange in specific discharge (ΔQ, mm h^{-1}), the maximum change in isotopic composition of the streamwaterstream water (δ^{2}H, ‰), and the minimum and maximum fraction of the catchment that was connected (A_{min}-A_{max}) during the event, and the date of the groundwater and soil water sampling campaign.

Event	Start date	*D* [h]	*P* [mm]	I_p [mm h^{-1}]	$I_{p\text{-}max}$ [mm h^{-1}]	*ΔQ* [mm h^{-1}]	*Q-δ^{2}H* [‰]	A_{min}-A_{max} [-]	*Date of sampling campaign*
I	02 Oct 2016	14	17	1.2	7	0.02 – 0.07	-70.5 to -65.7	0.27 – 0.48	05 Oct. 2016
II	25 Oct 2016	28	33	1.2	13	0.02 – 0.17	-75.3 to -67.6	0.27 – 0.35*	05 Oct. 2016
III	03 Oct 2017	7	27	3.9	24	0.08 – 0.43	-73.7 to -69.1	0.33 – 0.68	12 Oct. 2017
IV	05 Oct 2017	27	32	1.2	10	0.07 – 0.30	-69.1 to -65.2	0.33 – 0.67	12 Oct. 2017

***The fraction of the catchment that was hydrologically connected increased from 0.27 to 0.28 during the sampling period, and to 0.35 during a discharge peak that occurred after the samplers stopped (see S3S2).**

Table 2. Average concentrations (± standard deviation) for all groundwater (GW_{avg}; n=335), all riparian groundwater (G1; n=99) and all hillslope groundwater (G2; n=99), soil water (SW; n=116), and rainfall samples (P; n=156). Solutes are ordered by their respective groups (section 4.3; Figure 6). Different superscript). Superscript letters [a-de] indicate the significantly different average concentrations.

Solute	Unit	GW_{avg}	G1	G2	SW	P
$\delta^{18}O$	‰	-11.0±0.9 [a]	-10.8±1.0 [ab]	-10.9±1.1 [ab]	-10.4±1.6 [ab]	-12.3±4.0 [ed]
δ^2H	‰	-76.0±7.5 [ba]	-74.3±8.0 [abadb]	-74.9±9.1 [ababd]	-70.8±12.4 [abd]	-84.4±33.0 [ed]
D_{ex}	‰	12.0±0.8 [a]	12.4±0.8 [ab]	11.8±0.9 [aab]	12.0±2.4 [aab]	14.1±3.2 [bc]
Cl	µg L^{-1}	830.8±1076.5 [a]	708.8±570.1 [a]	890.5±804.9 [aba]	1070.3±1026.6 [abb]	327.1±348.7 [c]
Zn	µg L^{-1}	593.9±1745.7 [aba]	720.4±2218.7 [a]	698.5±843.8 [abb]	23.3±12.5 [eb]	19.3±43.0 [c]
Cd	µg L^{-1}	0.05±0.08 [aead]	0.0±0.1[a]1 [ac]	0.1±0.1 [b]	0.03±0.06 [ac]	0.1±0.2 [bed]
Ni	µg L^{-1}	3.2±4.1 [da]	1.7±1.4 [abb]	5.6±6.6 [c]	2.5±1.5 [ada]	0.3±0.3 [bd]
Na	µg L^{-1}	1587.6±2672.7 [ba]	1107.1±1000.8 [ab]	827.6±341.3 [aeb]	839.1±565.0 [aeb]	148.7±153.5 [c]
Mg	µg L^{-1}	2235.7±1730.3 [a]	1292.5±684.3 [abb]	1164.1±435.6 [abb]	13612.8±10924 [c]	26.6±18.9 [bd]
Ca	µg L^{-1}	56993.7±21966.1 [ba]	44794.0±17097.6 [ab]	55624.6±18099.0 [ba]	22261.7±27287.8 [c]	213.4±202.7 [d]
Ba	µg L^{-1}	99.2±171.6 [a]	64.2±115.2 [ab]	112.3±258.6 [a]	37350±27637 [bc]	4.8±11.8 [ad]
Co	µg L^{-1}	0.8±1.05 [a]	1.1±1.0 [a]	0.3±0.2 [beb]	0.9±1.1 [a]	0.02±0.02 [c]
Cu	µg L^{-1}	64.9±143.7 [ea]	7.4±16.1 [ab]	175.5±211.8 [bc]	5.2±9.0 [ab]	1.4±1.0 [ad]
SO_4	µg L^{-1}	3600.0±5112.5 [ba]	2511.6±2843.2 [aba]	2418.7±1848.2 [aba]	1602.0±3061.9 [aeb]	623.1±980.1 [c]
K	µg L^{-1}	530.1±428.0 [bea]	328.3±219.2 [abb]	670.3±543.4 [eda]	754.1±970.8 [ea]	92.2±91.9 [ad]
Fe	µg L^{-1}	390.7±1271.1 [aba]	608.3±1648.4 [ab]	25.4±38.6 [ba]	254.3±775.9 [aba]	3.5±7.1 [bc]
Mn	µg L^{-1}	592.4±1111.6 [ea]	1007.8±911.3 [ab]	68.4±100.5 [bc]	139.9±326.2 [bc]	1.3±1.4 [be]

Table 3. Summary of the groups of the presented solutes (A-D, based on the relative concentrations ~~during~~computed for all four events; Fig. 6; ~~NG~~- indicates that this solute is not assigned to a group), the typical response of solute concentrations to increasing discharge (++: strong enrichment, mean R_x > 1.5; +: enrichment, mean R_x between 1 and 1.5; -: dilution, mean R_x < 1; ±: mixed response) and ratios between the average concentrations in soil water (C_{SW}) and groundwater (C_{GWavg}) and the groundwater from ~~riparian wells (C_{G1}) and~~ hillslope wells (C_{G2}) and riparian wells (C_{G1}) (see Table 2). See Fig. 5 and 6 for example concentration -and discharge relations for each group of solutes. The solutes are sorted according to their typical response.

Solute	D_{ex}	Cl	Fe	Mn	Co	Cu	SO_4	K	Cd	Zn	Ni	Na	Mg	Ca	Ba
Group	-	-	D	D	C	C	C	C	A	A	-	B	B	B	B
Typical [C] response to increasing Q	++	++	±	±	±	±	±	±	±	±	±	-	-	-	-
Ratio C_{SW}/C_{GWavg}	1.0	1.3	0.7	0.2	1.1	0.1	0.4	1.4	0.6	~0	0.8	0.5	6.1	0.4	376.5
Ratio C_{G2}/C_{G1}	1.0	1.3	~0	0.1	0.3	23.7	1.0	2.0	-	1.0	3.3	0.7	0.9	1.2	1.7

~~Solute~~	~~Group~~	~~Typical [C] response to increasing Q~~	~~C_{SW}/C_{GWavg}~~	~~C_{G2}/C_{G1}~~
~~D_{ex}~~	~~NG~~	~~++~~	~~1~~	~~1~~
~~Cl~~	~~NG~~	~~++~~	~~1.3~~	~~1.3~~
~~Fe~~	~~D~~	~~±~~	~~0.7~~	~~~0~~
~~Mn~~	~~D~~	~~±~~	~~0.2~~	~~0.1~~
~~Co~~	~~C~~	~~±~~	~~1.1~~	~~0.3~~
~~Cu~~	~~C~~	~~±~~	~~0.1~~	~~23.7~~
~~SO_4~~	~~C~~	~~±~~	~~0.4~~	~~1~~
~~K~~	~~C~~	~~±~~	~~1.4~~	~~2~~
~~Cd~~	~~A~~	~~±~~	~~0.6~~	-
~~Zn~~	~~A~~	~~±~~	~~~0~~	~~1~~
~~Ni~~	~~NG~~	~~±~~	~~0.8~~	~~3.3~~
~~Na~~	~~B~~	-	~~0.5~~	~~0.7~~
~~Mg~~	~~B~~	-	~~6.1~~	~~0.9~~
~~Ca~~	~~B~~	-	~~0.4~~	~~1.2~~
~~Ba~~	~~B~~	-	~~376.5~~	~~1.7~~

~~**Table 4. Event-average pre-event water fraction (f_{pe}) based on the two-component hydrograph separation using δ^2H as a tracer, and the event**~~

Table 4. Event-average fractions of groundwater (f_{GW}), soil water (f_{SW}), and rain water (f_P), based on the three-component End-Member Mixing Analyses, the pre-event water fraction (f_{pe}) based on the two-component hydrograph separation using δ^2H as a tracer, and the associated uncertainties for both calculations.

Event	~~Two~~Three-component End-Member Mixing Analyses				~~Three~~Two-component ~~End-Member Mixing Analyses~~	
	~~f_{pe}~~f_{GW}	~~uncertainty~~f_{SW}	~~f_{GW}~~f_P	~~f_{SW}~~uncertainty	~~f_P~~f_{pe}	uncertainty
I	0.~~86~~69	~0.28	0.~~81~~31	~0.93	0.~~19~~91	0.16
II	0.~~76~~21	0.~~61~~33	0.~~49~~45	0.~~27~~60	0.~~24~~76	0.~~14~~31

III	0.~~81~~39	0.~~69~~38	0.~~72~~22	~~0.01~~1.59	0.~~27~~78	0.~~16~~35
IV	0.~~78~~72	~0~~.25~~	0.~~74~~28	~~0.01~~1.43	0.~~25~~97	0.~~14~~19