

Response to Reviewers – Point-by-point response to reviewer comments on “Concentration-discharge relationships vary among hydrological events, reflecting differences in event characteristics” by Julia L. A. Knapp et al.

We would like to thank two anonymous reviewers for helpful comments on our manuscript. The point-by-point reply to the comments is given below. The comments provided by the reviewers are shown in italics, and our responses in regular font in blue. Changes made to the manuscript are indicated by underlined text. Line numbers in the responses refer to the updated manuscript with tracked changes marked.

Contrary to the reply we posted to the comments from reviewer #1, we will use the term “two-year” to describe the results from the full dataset, to follow the recommendations by the editor.

Please note that we have also had to update our dataset due to a registration error in the discharge timeseries, which resulted in a shift of one hour for all data points. This does not affect the interpretation of our results, but changes all numbers by the second or first decimal. We have therefore updated all figures and tables in the manuscript.

1) Response to the interactive comment of Reviewer #1

General comments:

This study examines the concentration-discharge (c-Q) relationships of several solutes at the scale of individual storm events and across the entire two-year study period in the Swiss Erlenbach catchment. The authors use the similarities and differences among solute c-Q slopes and intercepts to make inferences about the timing and hydrologic sources of streamwater in the catchment. The study also correlates the c-Q slope and intercept values with a wide variety of environmental controls to identify the most important regulators of solute transport within the Erlenbach catchment. I commend the authors for undertaking a sampling regime intense enough in both its frequency and duration to permit the development of such a unique dataset. High-frequency precipitation and stream sampling can be difficult during a single event, not to mention across multiple events. It is unfortunate that the nature of the Erlenbach catchment's hydrology was such that the study's sampling regime could not fully capture the c-Q responses across the complete hydrograph of the sampled storms. However, the authors made a convincing case for constraining their analysis to only the recession limb data, and they were mostly careful to not extent their inferences beyond where their limited dataset would allow them to go. I include the caveat “mostly” because I do question the description of a two-year, growing season only dataset as “long-term”. This is perhaps a minor quibble, but I think it would be more accurate to describe the full dataset as “interannual” rather than “long-term”. Overall, the authors present an interesting study of c-Q relationships at the catchment scale, highlighting important differences in biogeochemical responses observed across a range of temporal scales. This manuscript may be acceptable for publication in HESS, provided the authors address the specific comments outlined below.

We thank the reviewer for her/his positive assessment of our study. We understand the concerns regarding the term “long-term” for a two-year data set. The terminology was intended to more clearly separate observations based on the longer dataset from those

of individual hydrologic events. Nevertheless, we understand that it may be misleading. Following the recommendation from the editor, we use the term “two-year” instead in the revised version.

Specific comments:

L99: How long did the precipitation funnel sit out in the open prior to the onset of rainfall? I am curious whether some of the solute concentrations in the early precipitation samples during events might have been biased by the addition of dry deposition on the funnel surface.

The collection and analysis of precipitation was automated, like the streamwater sampling. Therefore, the funnel was not cleaned and rinsed before every sample. However, rainfall events at Erlenbach occur roughly every second day, and the effect of dry deposition accumulating on the funnel was likely small. To account for the effect of dry deposition, we used (rainfall-) volume-weighted precipitation concentrations in our calculations (Tables 1 and 2). Small-volume samples at the start of a rain event with high solute concentrations due to dry deposition therefore had little weight in the calculation. Furthermore, our analysis is mostly based on the streamwater samples. The precipitation samplings procedure is described for completeness, and because the solute concentrations in precipitation are investigated as potential environmental drivers to explain the observed cQ slopes and intercepts (sections 2.6 and 3.4).

L121-122: Related to my previous comment, I'm curious how often it was the case that the first precipitation sample collected during an event was classified as an outlier. It might not affect your overall results much, but depending on how important a source dry deposition is in the study catchment, it might be worth considering. Also, I think it's important to provide additional details about the identification of outliers in the dataset. Was there a threshold that you set, or did you truly just “eyeball” the dataset? For example, how did you identify outliers in the case of solutes that had more variable (less tight) spreads? What proportion of the entire dataset was identified as outliers?

We excluded very few precipitation samples from our analysis, usually only if there was a known problem with the precipitation collector. Precipitation solute concentrations were generally very variable, even within an individual rain event. Generally, we observed a gradual decrease in solute concentrations as the rain event progressed. A possible explanation of this gradual decrease in precipitation solute concentrations could be due to the wash-off of dry deposition from leaves and the rain-out of aerosols in the atmosphere, and therefore likely reflect the normal processes occurring in the landscape.

Eliminating outliers in streamwater samples was mainly based on visual inspection. During the hydrograph recession, solute concentrations at Erlenbach generally change gradually from sample to sample (given our very high sampling frequency). Sudden jumps and outliers due to anomalous instrument behavior or sample handling were therefore often easy to detect. We furthermore compared among solute groups and instruments. Suspected anomalies in cation and anion data were compared across instruments, and if these anomalies were inconsistent across instruments, the respective data points were removed. We were generally very conservative in the removal of outliers.

L125 and L134: The word “aggregated” is kind of vague. Does this mean you averaged the data? Calculated the median?

Because streamwater sampling is instantaneous (not composite) in our field laboratory, we picked the closest 10-min data point for any quantity related to streamflow (discharge, EC in streamwater), air temperature and groundwater level. For the precipitation samples, the 10-min precipitation rates were cumulated from the start of the event or the last sampling time until the time of sampling. We clarify this in the revised manuscript: “For the purpose of this study, only every second EC measurement was used to match the 10-min measurement frequency of river discharge” (lines 128-129), and “For this purpose, we extracted those data that were closest to the sampling times of each streamwater sample from the 10-minute discharge, air temperature, and groundwater level time series. For the precipitation samples, associated precipitation amounts were calculated as cumulative sums from the 10-minute tipping bucket recordings.” (lines 138-140)

L174-175: Did you consider how this flux index might be affected by accumulated dry deposition on your precipitation collector? This would be more important for some ions (e.g., nitrate, chloride, maybe sulfate) compared to others.

Acknowledged. It is indeed possible that dry deposition affected the flux budgets. However, dry deposition of soluble compounds *should* be part of the flux budgets, since they are real input fluxes that need to be taken into account if one wants an accurate picture of whether the catchment is a net source or sink of the solutes in question. In any case the effect should be small; given that it rains frequently at Erlenbach, the amount of dry deposition was probably relatively negligible (see explanation above).

L205-210: How many of the 30 events that you sampled fell into the category of being “not well constrained”? I can understand why you would want to limit your analysis to only those events for which the c-Q relationships were relatively straightforward, but this approach also kind of seems a little like “cherry picking” to me... From a practical standpoint, I completely understand the need to make such decisions about whether and when to exclude data (assuming they constitute a small percentage of the overall dataset) but I wonder if by limiting your dataset in this way, it also means that you’re excluding some potentially important information about biogeochemical processes at event timescales. Those high RSEs are caused by something, and if they are attributable (even in part) to environmental and/or hydrologic drivers, there could be some very useful insights to be mined out of that variability.

Acknowledged. We excluded cQ relationships from events and solutes with high relative standard error (RSE) because they did not allow us to fit a power-law relationship, and thus would not allow for a consistent interpretation of the recession behavior. Nevertheless, we understand the concern that we may be excluding potentially important information. We thus redid the analysis with all calculated slope and intercept values (weighted by the inverse of the respective RSE) and we obtained a very similar result of the correlation analysis shown in Figure 5 of the manuscript.

The number of events excluded due to high RSEs was small for most solutes (usually none, and a maximum of 7 out of the 30 events), except manganese and copper (for which 13 and 17 events out of the 30 events had to be excluded because of high RSE, respectively). The generally low concentrations of these two solutes had high fractional variability, resulting in no clear power-law relationship for many events. We include a note on this in the revised version of the manuscript: “More than 20 events were evaluated for all other solutes, except manganese and copper. The concentrations of these two solutes were low and variable, resulting in no clear power-law relationship with discharge for many events. Consequently, only data from 17 and 11 events were usable for manganese and copper, respectively.” (lines 251-254)

L678-680 (Figure 4): Somewhat related to the previous comment: do you see smaller uncertainties within events relative to the variability between events because you have removed from your analysis the storms with elevated RSEs?

This is a valid concern. We have added a copy of Figure 4 (see figure below) including the uncertainties in slope and intercept of all events in the supplemental material, even those excluded from further analysis. We provide a note on this in the caption of Figure 4 in the main text. As you can see, this mostly does not invalidate our statement that “the uncertainty in the estimated slopes and intercepts is mostly smaller than the variability between events, ...”. An exception may be manganese.

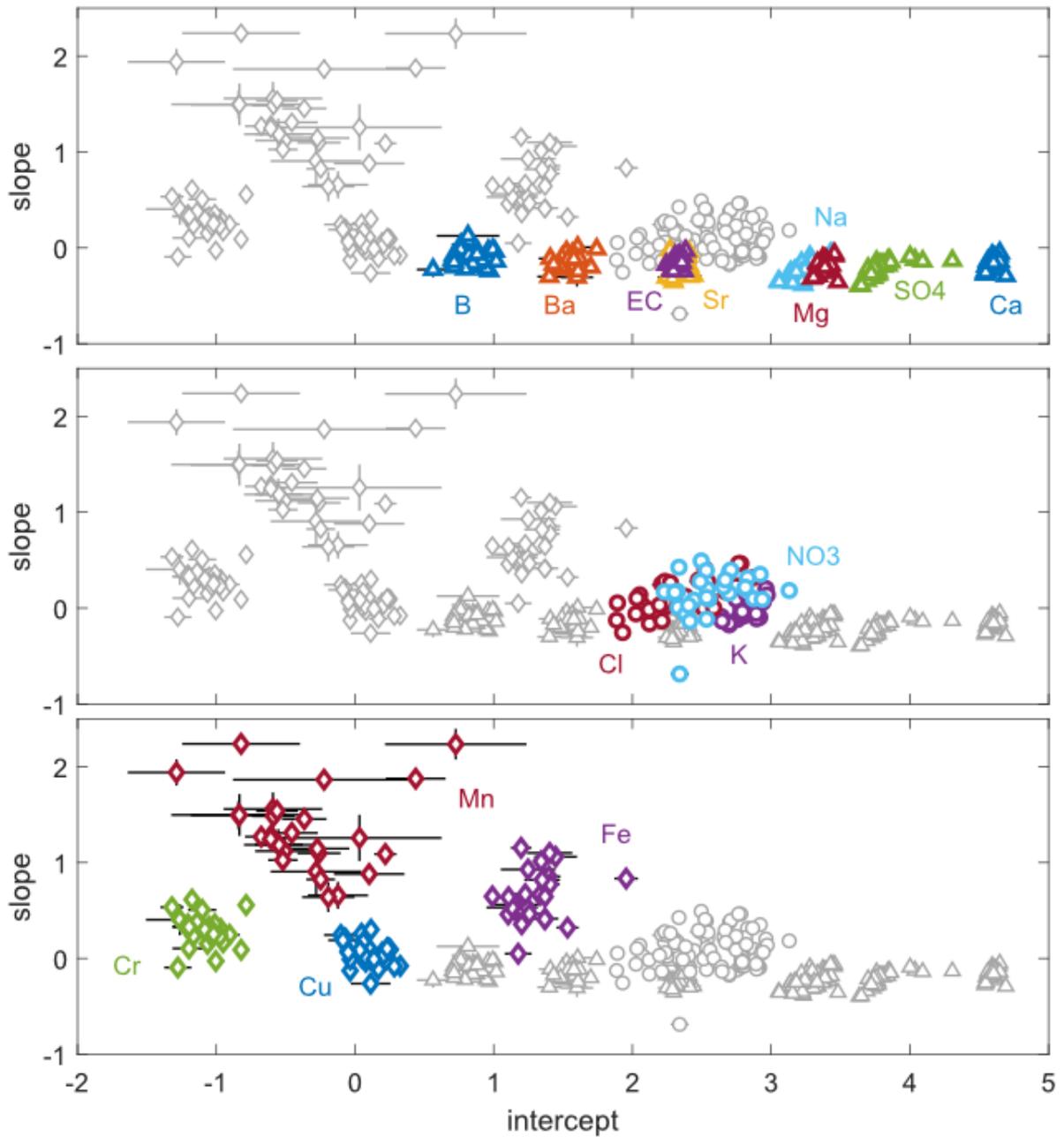


Figure 4 updated. Scatter plots of event cQ slopes and intercepts of the 14 different solutes and EC (error bars indicate one standard error). Solutes from different dominant sources cluster and exhibit similar ranges of variability. (a) Groundwater-sourced solutes cluster closely around similar slopes and show little inter-event variability in both slopes and intercepts. (b) Intercepts and slopes of solutes with significant atmospheric input (i.e., chloride, nitrate, and potassium) vary substantially among events. (c) The slopes of trace metals are generally higher than those of the other solutes (indicating predominantly mobilization behavior), and are also highly variable among events. The uncertainty in the estimated slopes and intercepts is mostly smaller than the variability between events, indicating that the observed inter-event variability in slopes and intercepts reflects real-world behavior rather than sampling and measurement noise.

2) Response to the interactive comment of Reviewer #2

General comments:

This is a well written, well presented, and interesting study on the cQ relationships of 14 different solutes in the Swiss Erlenbach catchment. The study sheds new light on the variability of these relationships among individual hydrological events. The resulting patterns and contrasts among the various solutes are clearly visualized. Perhaps the only shortcoming of this study is the lack of some more data/information like pH to better understand the role of biogeochemical processes in controlling the cQ relationships. This study calls for research to further link such patterns with detailed biogeochemical process studies and hypotheses.

We thank Reviewer #2 for her/his positive comments on our manuscript. Please find our responses regarding additional data below.

Specific comments:

1. Introduction: already shed some light on the measurement approach (automated field lab) near the end of the introduction as it remains puzzling for the reader at the objectives how then such high resolution datasets were obtained for so many events.

Accepted. We will add a sentence at the end of the introduction mentioning the automated field laboratory: “In this study we analyzed high-frequency measurements of 14 different solutes ranging from major ions to trace metals that we obtained from an automated field laboratory set up at the outlet of a pre-Alpine catchment (von Freyberg et al., 2017). We quantified multi-year cQ relationships from the snow-free periods of a 2-year data set,...” (lines 73-75)

2. Section 2.2. Dataset: I miss information on some essential parameters like silica, alkalinity, and pH:

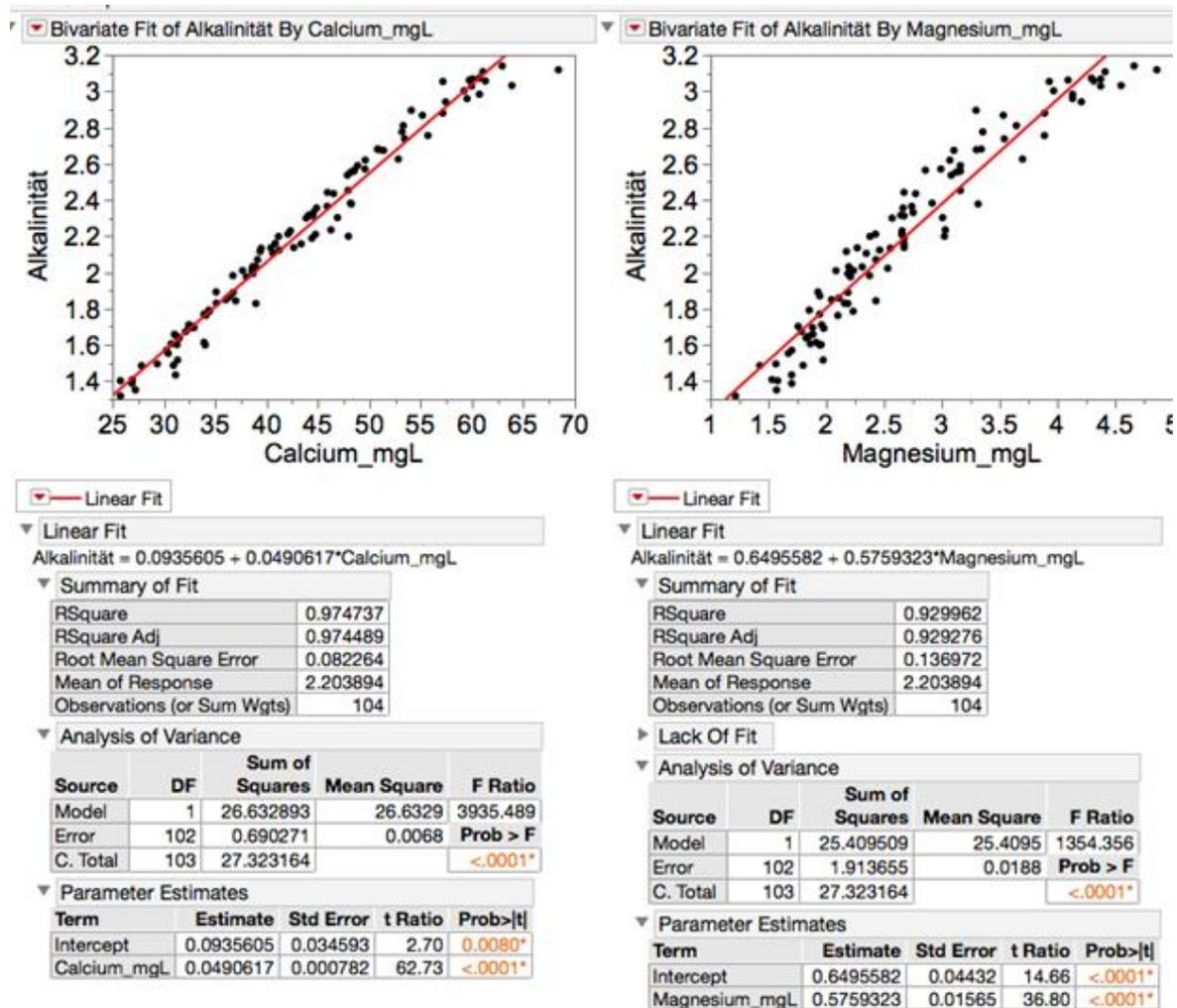
a. Was silica measured by ICP-MS but below detection? That seems surprising. Or was it not measured, or perhaps not feasible with ICP-MS? Because silica is usually a very useful element in cQ studies.

Acknowledged. We did not measure silica, because only a small part of it is available in dissolved form. The majority is present in streamwater as colloid polysilicic acid and is thus filtered out during the pre-processing of the sample.

b. Why was Alkalinity not also measured? Or at least perhaps on weekly basis when the lab in the field was visited and samples collected? Some background information on Alkalinity is welcome to better understand the biogeochemistry in this catchment. Only towards the end of the paper is it suggested that bicarbonate is the main (counter)anion (line 406).

Alkalinity was not measured at high frequency because this measurement could not be automated and thus not measured in our field laboratory set-up. Within the “National Long-term Surveillance of Swiss Rivers” (NADUF), a composite streamwater sample is collected weekly and analyzed for major ions at the Erlenbach outlet. Based on NADUF data from 2017 and 2018, we find that alkalinity is strongly correlated with calcium and magnesium concentrations at Erlenbach (see figure below), and thus relationships

between alkalinity and discharge would likely be very similar to those observed for calcium and magnesium. We agree that some information on the expected chemistry at the site would be helpful. We will include the following text in the site description: “The underlying geologic formation is Flysch, and the highly layered bedrock consists of limestone, claystone, marl, and shale, as well as conglomerate and calcareous sandstone... Groundwater chemistry is thus dominated by calcium, magnesium, and their counter-anion, bicarbonate.” (lines 84-85)



c. Why was pH not measured with a sensor alike EC? Same request as for Alkalinity: some information is helpful for better understanding. Furthermore, variations in pH may be highly relevant to better understand variations in trace metals like Fe, Mn, Cr. This could also be added to the discussion/outlook. pH sensors I think should be sure be included in a downsized toolbox as discussed in section 5.

pH was measured at the same frequency as EC in streamwater. However, we experienced problems with the pH sensor after May 2018, so we refrain from using pH measurements in our analysis. At Erlenbach, streamwater pH is buffered due to the high concentrations of bicarbonate and varies between 7.6 and 8.3. Short-term drops in pH can be observed during precipitation events, with quick recovery to the initial pH values as soon as rainfall stops.

We had initially analyzed pH, but found no behavior comparable with any of the trace metals (i.e., no similar sensitivities of pH and any trace metals to environmental controls). The cQ slopes and intercepts of the trace metals were also not related to any metric calculated from pH (relative or absolute change in pH during the event, cQ slope of pH etc. tested as environmental control). Instead, those metrics seemed to be more closely related to the patterns of the groundwater solutes (e.g., Ca, Mg, Na). We believe this is because the mobilization of trace metals is related to soil pH at the relevant location, but this can differ substantially from the pH variations observed in streamwater. Also, streamwater pH is probably buffered substantially by bicarbonate, which is groundwater-derived. Consequently, variations in streamwater pH do not seem related to the mobilization of trace metals. However, we acknowledge that this may be different in other, less buffered systems. We will consequently add the following statement to the outlook in Section 5 (please also see comment #9): “... suitable proxy for iron and some other trace metals. pH measurements may also provide helpful insights into the mobilization of trace metals from soil layers.” (lines 496-497)

3. Section 3.1. Dataset:

lines 240-245: what is meant with “sufficient .. measurements” and “were analysable”? Is it meant that samples with concentrations below the detection limit could not be used?

No, but because ICP-MS analysis was only performed on every second sample, fewer concentration data were available for these solutes. If any of these few data points had to be excluded because it was identified as an outlier, this resulted in a number of event recessions with fewer than the required 5 measurements for these solutes. Furthermore, specific solutes and events were excluded, because the relative standard errors of the cQ slopes or intercepts were too high. We will clarify this in the revised version of the manuscript by changing the sentence to: “While IC measurements were available for all 30 hydrologic events, not all events had the required 5 sample points for all of the cations analyzed by ICP-MS (i.e., boron, barium, iron, manganese, chromium, strontium, and copper). Furthermore, some events had to be excluded from further analysis for individual solutes due to high relative standard errors of cQ slopes and/or intercepts (see Sect. 2.5). This resulted in 24 to 30 usable events for major ions measured with the IC. More than 20 events were evaluated for all other solutes, except manganese and copper. The concentrations of these two solutes were low and variable, resulting in no clear power-law relationship with discharge for many events. Consequently, only from 17 and 11 events were usable for manganese and copper, respectively.” (lines 246-254)

4. Section 3.2. Line 269: Clarify which solutes precisely are meant with “these solutes” and at line 266 with “weathering products”. All the aforementioned solutes in this paragraph, or only Mg/Na/SO₄?

The statement regarding a heterogeneous distribution of groundwater solutes was intended to include all groundwater solutes, not just Mg/Na/SO₄. We will make this clearer by amending the text as follows (lines 265-269): “In general, groundwater concentrations of weathering products are likely to be highly heterogeneous in the Erlenbach catchment due to spatially variable contributions from the geochemically complex Flysch bedrock... Precipitation concentrations of these weathering products are low,...” (lines 275-279)

5. *General comment about Fe levels and its redox state (also in relation to lines 378-379: nanoparticulates of trace metals). As pH is not provided it is difficult to better understand the Fe chemistry. Under acidic conditions the Fe could be leached from soil as Fe(III) and kept as ion in solution but at higher pH and also when Fe partially occurs as Fe(II) (after reduction in organic rich soils?) one would expect oxidation to Fe(III) in the stream and subsequent formation of (micro) iron flocs that might be removed by the automated field lab that filtrates the samples prior to ICP-MS analysis. Were also non-filtered samples analysed on Fe now and then to conclude anything on the potential role of particulate iron oxides in the stream? And how this may have affected cQ relationships?*

pH at the Erlenbach was always above 7.6 and ranged up to 8.2. As pointed out by the reviewer, the presence of (micro) iron flocs in streamwater is likely, and these may have been removed during filtration. Unfortunately, unfiltered water samples have not been analyzed, because filtration is an automatic step in our setup, and because the ICP-MS is easily damaged when analyzing unfiltered streamwater samples, as these are usually highly turbid particularly at times of interest (i.e., when flow is high).

6. *Lines 346-348: what about the potential role of spatially and temporal varying evapotranspiration and also dry deposition?*

Agreed. We will add an explanation to the manuscript: "... may result from varying degrees of atmospheric deposition, evapotranspiration, and dry deposition, resulting in temporally and spatially variable concentrations of chloride,...." (line 357)

7. *Line 358: Clarify what it meant with Fe and Mn bound to organic material? Is meant that Fe and Mn as ions are bound (only?) to organic material? Can Mn and Fe not also or perhaps more importantly occur in the soils as Mn- and Fe-oxide minerals?*

Agreed. We will re-formulate this as "... where they are bound to organic material or present as oxides." (line 370)

8. *Lines 419-429: This part of the discussion on the behaviour of trace metals may profit from further discussion and information on the role of temperature (rate of microbial reactions; temperature dependent sorption of trace metals) and redox conditions (does wetting for example lead to suboxic conditions deeper in these soils?). Also information on the pH variations would be very welcome to better understand the metal behaviour.*

Acknowledged. We agree that the factors mentioned by the reviewer are important for the mobilization of metals from soils. Unfortunately, we have no spatial information on soil temperature, redox conditions, or soil pH. We will, however, include a note on this at the end of the paragraph as suggested: "As metal complexation and mobilization is known to depend on various factors such as pH and redox conditions in the soil layer (Gotoh and Patrick, 1972, 1974), further field measurements are necessary to better understand the mobilization of trace metals from soil layers during hydrologic events." (lines 441-444)

9. Section 5: lines 475-481: especially in relation to understand metal behaviour employing also a pH sensor is essential.

Agreed. We will add the following in the revised manuscript: "... The analysis of trace metals is not available through automated sensors, but in many cases DOC can be a suitable proxy for iron and some other trace metals. pH measurements may also provide helpful insights into the mobilization of trace metals from soil layers." (Please also see our response to comment #2c)

3) Referenced Literature

Gotoh, S., and Patrick, W. H.: Transformation of Manganese in a Waterlogged Soil as Affected by Redox Potential and pH. *Soil Science Society of America Journal*, 36(5), 738-742, 1972.

Gotoh, S., and Patrick, W. H.: Transformation of iron in a waterlogged soil as influenced by redox potential and pH. *Soil Science Society of America Journal*, 38(1), 66-71, 1974.

von Freyberg, J., Studer, B., and Kirchner, J. W.: A lab in the field: high-frequency analysis of water quality and stable isotopes in stream water and precipitation, *Hydrol. Earth Syst. Sci.*, 21, 1721-1739, <https://doi.org/10.5194/hess-21-1721-2017>, 2017.

Concentration-discharge relationships vary among hydrological events, reflecting differences in event characteristics

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10 **Abstract.** Studying the response of streamwater chemistry to changes in discharge can provide valuable insights into how catchments store and release water and solutes. Previous studies have determined concentration-discharge (cQ) relationships from long-term, low-frequency data of a wide range of solutes. These analyses, however, provide little insight into the coupling of solute concentrations and flow during individual hydrologic events. Event-scale cQ relationships have rarely been investigated across a wide range of solutes and over extended periods of time, and thus little is known about differences and
15 similarities between event-scale and long-term cQ relationships. Differences between event-scale and long-term cQ behavior may provide useful information about the processes regulating their transport through the landscape.

Here we analyze cQ relationships of 14 different solutes, ranging from major ions to trace metals, as well as electrical conductivity, in the Swiss Erlenbach catchment. From a 2-year time series of sub-hourly solute concentration data we
20 determined ~~long-term~~two-year cQ relationships for each solute and compared them to cQ relationships of 30 individual events. The ~~long-term~~two-year cQ behavior of groundwater-sourced solutes was representative of their cQ behavior during hydrologic events. Other solutes, however, exhibited very different cQ patterns at the event ~~and long-term~~-scale and across two consecutive years. This was particularly true for trace metals as well as atmospheric and/or biologically active solutes, many of which exhibited highly variable cQ behavior from one event to the next. Most of this inter-event variability in cQ behavior can be
25 explained by factors such as catchment wetness, season, event size, input concentrations, and event-water contributions. We present an overview of the processes regulating different groups of solutes, depending on their origin in and pathways through the catchment. Our analysis thus provides insight into controls on solute variations at the hydrologic event scale.

1 Introduction

30 The movement of water and solutes through the landscape is inherently coupled. Streamwater chemistry at a catchment outlet differs depending on the flowpaths of water through the catchment and can therefore be considered a “fingerprint” of catchment transport, mixing, and reaction processes. Consequently, studying the response of streamwater chemistry to changes in discharge provides insight into how catchments store and release water and solutes. Changes in solute concentrations as functions of discharge, i.e., concentration-discharge (or cQ) relationships, have commonly been assessed using multi-year time series of low-frequency (weekly to monthly) streamwater chemistry measurements (Hall, 1970; Godsey et al., 2009; Musolff et al., 2015; Godsey et al., 2019). At this temporal scale, cQ relationships can serve as indicators of hydrologic and biogeochemical processes. Decreasing solute concentrations with increasing flow (often referred to as “dilution behavior”, Fig. 1a) have frequently been associated with source limitations, indicating the depletion of finite solute sources in the catchment (Basu et al., 2011) or mixing with more dilute waters. Conversely, patterns of increasing solute concentrations with discharge are described as “mobilization behavior” resulting from the flushing of solutes, for example from upper soil layers (Fig. 1c). Solute concentrations that vary little across wide ranges of discharge (“chemostatic behavior”, Fig. 1b) can result from several mechanisms, including the storage and release of solutes that are not supply limited (Godsey et al., 2009; Basu et al., 2011), the over-printing of source-limitation and mobilization behavior (Cartwright et al., in press), or from large pre-event water contributions to storm runoff (Clow and Mast, 2010).

45 Because cQ relationships can vary between solutes and catchments, they are frequently employed as descriptors for catchment hydrological behavior. The cQ relationships obtained from long-term, low-frequency data are particularly useful for characterizing the average behavior of a catchment (Clow and Drever, 1996; Godsey et al., 2009; Godsey and Kirchner, 2014). However, these long-term cQ relationships provide limited insight into the coupling of streamwater chemistry and discharge on shorter time scales, such as during hydrologic events. To better understand hydrologic controls on hydrochemical processes during events requires high-frequency hydrochemical observations, ideally spanning many contrasting storms. High-frequency streamwater sampling is cost- and labor-intensive, and thus most studies are limited to the characterization of individual hydrologic events (the study by Rose et al., 2018, is a rare exception). Recent technological progress in the development of in-situ sensors now allows for several solutes to be monitored at sub-hourly time scales (Rode et al., 2016). Analyses of these high-frequency measurements have provided substantial insights into biogeochemical processing (Rusjan et al., 2008), solute dynamics (Evans and Davies, 1998; Schwientek et al., 2013), and the temporal evolution of source contributions over the course of individual storm events (Grimaldi et al., 2004). Event-scale studies have also highlighted a general variability in solute responses across storm events that exceeds the variability observed in weekly or monthly grab samples (Bieroza and Heathwaite, 2015; Lloyd et al., 2016). These findings suggest that the controls on solute storage and transport processes on the event scale may be fundamentally different from those that shape long-term behavior.

Widely available chemical data from in-situ sensors are limited to a handful of solutes, including nitrate, orthophosphate, and dissolved organic matter. While these solutes provide interesting insights into different aspects of catchment processes (Carey et al., 2014; Dupas et al., 2016; Koenig et al., 2017), they are unlikely to characterize all relevant processes regarding solute mobilization from different parts of the catchment. Furthermore, event-scale cQ behavior is usually not placed into the context of long-term cQ behavior, because streamwater chemistry has rarely been measured at high temporal resolution over long periods. For example, solute concentrations during successive events in wetter years have been shown to be lower than in drier years (Biron et al., 1999), and events in wetter conditions may result in stronger surface water acidification than events following drier conditions (Wellington and Driscoll, 2004). However, because these studies measured solute concentrations only during individual events, we have no information on the long-term cQ behavior at these sites. Thus it remains challenging to identify controls of cQ behavior on both the event scale and longer time scales.

In this study we used high-frequency measurements of 14 different solutes ranging from major ions to trace metals that we obtained from an automated field laboratory set up at the outlet of a pre-Alpine catchment (von Freyberg et al., 2017). stream over a period of 2 years. We quantified the long-term two-year cQ relationships using from the snow-free periods from the of a entire 2-year data set, and compared them to event-scale cQ relationships of 30 hydrologic events that differed in size, antecedent wetness conditions, and seasonality indicators. Our study aims to explore questions such as 1) how does long-term two-year cQ behavior differ from cQ behavior observed on the event scale? 2) how variable are cQ relationships between individual events? and 3) can inter-event variability in cQ relationships be explained by specific environmental controls?

80 **2 Data and methods**

2.1 Site description

The Erlenbach catchment is a small (0.7 km²), steep catchment spanning an elevation range from 1100 to 1655 m above sea level in the northern Swiss pre-Alps. The underlying geologic formation is Flysch, and the highly layered bedrock consists of limestone, claystone, marl, and shale, as well as conglomerate and calcareous sandstone (Zobrist, 2010). Groundwater chemistry is thus dominated by calcium, magnesium, and their counter-anion, bicarbonate. The bedrock is overlain by umbric Gleysols with high silt and clay content in the steeper areas (Schleppi et al., 1998; Xu et al., 2009), and by mollic Gleysols with a permanently reduced B_g horizon in the flatter areas (Hagedorn et al., 2000). The catchment landscape is characterized by interchanging slopes and plateaus, and the groundwater table is generally shallower under the plateaus than under the slopes (Rinderer et al., 2014). The soil and bedrock permeabilities are relatively low, resulting in highly saturated soils, particularly on the plateaus. In total, 53 % of the catchment is forested, and dry and wet meadows cover roughly 14 and 33 % of the catchment area, respectively (van Meerveld et al., 2018). Coniferous forests cover the majority of the slopes, whereas meadows and partially forested areas can be found on the plateaus. Agricultural influence is limited to summer-season cattle grazing in the upper part of the catchment. Average annual precipitation in the Erlenbach catchment is 2300 mm, of which up to 40 %

falls as snow in the winter months (Stähli and Gustafsson, 2006), and about 20 % of incoming precipitation leaves the catchment as evapotranspiration (van Meerveld et al., 2018). In the years 2017 and 2018, stream discharge at the catchment outlet ranged from 0.2 to 2240 L s⁻¹, with an average value of 37.7 L s⁻¹.

2.2 Dataset

Streamwater and precipitation chemistry were analyzed semi-continuously by an automated field laboratory located at the Erlenbach catchment outlet (von Freyberg et al., 2017; von Freyberg et al., 2018). Streamwater was pumped continuously from the stream to the field laboratory, and precipitation was collected with an open 45 cm diameter funnel. During periods without rain, the field laboratory received only streamwater for analysis. The field laboratory analyzed precipitation whenever more than 50 ml of precipitation accumulated in the rain sampler (corresponding to roughly 0.3 mm of precipitation), and the previously analyzed sample was streamwater. A new sampling and analysis cycle was initiated every 30 minutes; thus, during rainfall, streamwater and precipitation samples were each analyzed hourly. A drift correction standard was analyzed instead of streamwater every 4 hours (every 6 hours after 12th March 2018).

Before analysis, each precipitation or streamwater sample passed through a 0.2 µm tangential filter. One aliquot of each sample was automatically directed to an ion chromatograph (940 Professional IC Vario, Metrohm AG, Herisau, Switzerland, hereafter referred to as “IC”) for the analysis of major anions and cations (calcium, magnesium, sodium, potassium, chloride, nitrate, and sulfate). Another aliquot was injected into a continuous water sampler module (CWS, Picarro Inc., Santa Clara, CA, USA) coupled to a cavity ring-down spectroscope (CRDS, Picarro Inc., Santa Clara, CA, USA) for water isotopes analysis (deuterium and oxygen-18). Further details on the sampling and analysis of isotopes and major ions in the field laboratory is described by von Freyberg et al. (2017) and von Freyberg et al. (2018).

In addition to the on-site analysis of major ions and stable water isotopes, aliquots of filtered rain water (every sample) and streamwater (one sample per hour) were automatically collected into vials. Each vial contained 1 ml of ultrapure HNO₃ to stabilize the water sample. These acidified samples were collected approximately once per week and brought to the laboratory at ETH Zurich for subsequent analysis of a wide range of trace elements using inductively coupled plasma mass spectrometry (Agilent 7900 ICP-MS, Agilent Technologies, Santa Clara, CA, USA, hereafter referred to as “ICP-MS”; more detail on the laboratory protocol can be found in the SI). Of the measured elements, we selected boron, strontium, barium, iron, manganese, copper, and chromium for further analysis in this study. The other elements were not included here because their concentrations were mostly below the analytical detection limits. Outlier removal of isotope, IC, and ICP-MS measurements was based on visual inspection.

Streamwater electrical conductivity (EC) was measured at 5-minute resolution (scan conductor, scan Messtechnik GmbH, Vienna, Austria). For the purpose of this study, only every second the EC measurement was used to match the data were aggregated to 10-minute intervals to match the measurement frequency of river discharge (see below).

130 River discharge was measured at a concrete flume installed at the Erlenbach catchment outlet (Hegg et al., 2006). Precipitation rates were recorded with a heated tipping-bucket rain gauge (Joss-Tognini 15183, Lambrecht meteo GmbH, Göttingen, Germany) at a meteorological station located at 1216 m above sea level in the Erlenbach catchment. At the meteorological station, air temperature was measured with a ventilated thermometer (VT3, Meteolabor AG, Wetzikon, Switzerland), and groundwater level fluctuations were recorded in a fully screened well (these readings were relative rather than absolute, 135 because they have not been calibrated against manual water level measurements). Discharge, precipitation, air temperature, and groundwater levels were recorded at 10-minute resolution. These data were aggregated to 30-minute or 1-hour intervals to match the frequency of the solute data, except for the analysis of the EC data, for which the 10-minute resolution was used. For this purpose, we extracted those data that were closest to the sampling times of each streamwater sample from the 10-minute discharge, air temperature, and groundwater level time series. For the precipitation samples, associated precipitation amounts were calculated as cumulative sums from the 10-minute tipping bucket recordings.

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2.3 ~~Long-term Dataset~~ dataset and event identification

The Erlenbach stream generally shows a fast and flashy response to rainfall events, resulting in very short durations of the rising limb of the storm hydrograph, in particular during short and intense events. Consequently, few samples were collected 145 during the rising limb of each storm in spite of the high sampling frequency of the field laboratory. The falling limb of the streamflow hydrograph, on the other hand, was generally well captured. For this reason, we excluded all samples collected during periods of increasing discharge from our analysis (in Sect. 3.3 below, we show that excluding these periods has negligible effects on the ~~long-term~~ two-year cQ behavior). The relationship between solute concentrations and streamflow during hydrograph recession is informative in particular on outflow processes from shallow and deeper groundwater, as well 150 as riparian water (Inamdar et al., 2006).

We excluded the winter months from the dataset to avoid ambiguities arising from rain-on-snow and snowfall events in our analysis, because solute responses to these events may differ from those during rain events in snow-free periods. Consequently, only data points between May 1st and November 15th in both 2017 and 2018 were analyzed (hereafter referred to as the “snow-free periods”). During these snow-free periods, we identified individual events based on the following criteria: (1) events had 155 to have a substantial increase in discharge, i.e. peak discharge at least 20 L s⁻¹ above pre-event baseflow; (2) this discharge increase had to be triggered by rainfall; (3) the hydrograph had to recede by at least 75% of the absolute increase in discharge

before the event was cut off (e.g. due to a subsequent rain event or sampler failure); and finally, (4) only events were considered for which IC (i.e., major ions) measurements were available.

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For each event, we analyzed the solute concentration and discharge data during the hydrograph recession, starting at the main discharge peak of an event until 95% hydrograph recession to baseflow, or until the event was cut off by the start of a subsequent event (if discharge had receded by at least 75%). We estimated cQ relationships for solute/event combinations for which at least 5 data points were available on the recession limb.

165 **2.4 Assessment of source-area concentrations and input-output budgets**

To identify likely streamwater sources, we quantified average solute concentrations of different compartments in the Erlenbach catchment: median solute concentrations in streamwater and precipitation and their lower and upper quartiles were calculated from the snow-free periods in the time series. Solute concentrations in groundwater were obtained from sampling two pumping wells in the upper part of the catchment at three different instances between 2016 and 2017. Although these groundwater chemistry data may not provide a comprehensive picture of Erlenbach groundwater, they can nonetheless indicate which solutes are likely to be dominant therein. Concentrations in soil water of the neighboring Studibach catchment were obtained from sampling eighteen suction lysimeters during eight baseflow snapshot campaigns in the snow-free season in 2016 and 2017 (detailed description of the campaigns are given in Kiewiet et al., 2019). We aggregated the data from six sites (three forested, three non-forested), spread over three elevations in the catchment (1361, 1502 and 1611 m above sea level), at which suction lysimeters were installed at 15, 30 and 50 cm depth. The lysimeters were emptied and set to a tension of 50 mbar the day prior to sampling.

We characterized the source-sink behavior of the Erlenbach catchment for individual solutes using a dimensionless solute flux index calculated from the high-frequency data of the snow-free periods. The solute flux index F relates solute fluxes in precipitation inputs I to those in streamwater outputs O :

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$$F = \frac{O - I}{\max(O, I)} = \frac{Q_{tot} \langle c_{Q_i} \rangle - P_{tot} \langle c_{P_i} \rangle}{\max(Q_{tot} \langle c_{Q_i} \rangle, P_{tot} \langle c_{P_i} \rangle)} \quad (1)$$

Where Q_{tot} and P_{tot} are the total streamflow and precipitation water fluxes, c_{Q_i} and c_{P_i} are the solute concentrations in streamflow and precipitation for all sampling times i , and the angled brackets indicate volume-weighted averages. The index is positive if the streamwater solute flux is larger than the precipitation solute flux, and quantifies the fraction of the output flux O generated within the catchment. Conversely, if the index is negative, it quantifies the fraction of the input flux I retained within the catchment. If the input and output fluxes are exactly balanced, the flux index will be zero. Importantly, the solute

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flux indices as calculated here provide no information on long-term fluxes, but relate the output and input fluxes during the snow-free periods between May and November from which the hydrologic events were extracted.

2.5 Quantification of concentration-discharge relationships

We estimated both the ~~long-term~~two-year cQ behavior (i.e., using all recession data from the snow-free periods in 2017 and 2018), and the individual event-scale cQ behavior by fitting power-law relationships between concentration c and discharge Q to the data (Clow and Drever, 1996; Musolff et al., 2015):

$$c = aQ^b \quad (2)$$

This power-law relationship is identical to a linear relationship in double-logarithmic space:

$$\log_{10}(c) = \log_{10}(a) + b \log_{10}(Q) \quad (3)$$

Where $\log_{10}(a)$ and b are the intercept and slope of the cQ relationship, respectively. cQ slopes and intercepts of the entire dataset will be referred to as “~~long-term~~two-year” cQ slopes and intercepts, whereas “event-scale” will refer to cQ relationships of individual hydrologic events. For the purpose of this study, we normalized discharge by the average discharge of the time series ($\log_{10}(Q/Q_{mean})$) to obtain ~~long-term~~two-year intercepts that reflect the expected concentration at the mean discharge, rather than the arbitrary value of $Q=1$ ($\log_{10}Q = 0$). Centering the x-axis in this way also has the benefit of making the slope and intercept estimates more independent from one another.

We calculated the relative standard errors of the event-scale slopes and intercepts, in order to exclude events for which the cQ relationships could not be well constrained. cQ relationships were excluded from our analysis if the relative standard error of either the cQ slope *or* intercept for any event and solute exceeded 50 %, or if both the relative standard error of the cQ slope *and* intercept exceeded 25 %.

Given that our samples represent chemistry of hydrograph recession, the meaning of the obtained cQ slopes can be interpreted as follows: a cQ slope of 1 (or -1) is obtained if changes in solute concentrations are proportional (or inversely proportional) to changes in discharge during recession. Consequently, a cQ slope between -1 and 1 indicates less-than-proportional changes in solute concentrations, and a cQ slope close to zero indicates solute concentrations that change relatively little, or that vary independently of discharge during recession. Conversely, cQ slopes greater than 1 indicate that solute concentrations decrease more-than-proportionally to discharge during recession. Examples of the relationships between cQ slopes, solute recessions, and hydrograph recessions are illustrated in Fig. 1.

2.6 Possible environmental controls of inter-event variability in cQ relationships

225 The 30 hydrologic events span wide ranges of storm durations, intensities, antecedent wetness conditions, and other potential controls, thus facilitating an investigation into how these environmental controls may influence the slopes and intercepts of the event-based cQ relationships. To this end, we quantified 15 different parameters for each event from the following five categories: (1) temperature and proximity to midyear as seasonality indicators; (2) relative input concentrations, which quantify the ratio between the volume-weighted average precipitation concentration during the event to the streamwater solute concentrations during pre-event baseflow; (3) groundwater levels, baseflow discharges, and antecedent precipitation as
230 indicators of antecedent wetness conditions; (4) several measures of event magnitude and intensity; and (5) event and pre-event water contributions determined from isotope hydrograph separation (following the approach presented by von Freyberg et al., 2018). Table 1 presents an overview of these 15 environmental controls, as well as their ranges in our dataset.

As a seasonality indicator, the proximity to midyear is calculated as a summer-winter index:

$$235 \quad SW = \begin{cases} \frac{doy}{182.5}, & doy < 183 \\ \frac{365 - doy}{182.5}, & doy \geq 183 \end{cases} \quad (4)$$

Where *doy* is the day of year. This summer-winter index approaches 0 at the beginning and end of each calendar year, and approaches 1 at the beginning of July.

We used weighted rank correlation coefficients to quantify the dependence of event-scale cQ slopes and intercepts on the 15
240 environmental controls. The weights were the inverses of the standard errors of the individual cQ slopes and intercepts, to prevent highly uncertain points from substantially influencing the results. The statistical significances of these correlation coefficients (their *p*-values) quantify the probability of obtaining an equal or greater correlation if the null hypothesis were valid (i.e., if there were actually no relationship between the slope or intercept and the respective control).

3 Results and discussion

245 3.1 Dataset

We extracted 30 events from the time series of 2017 and 2018 that fulfilled the criteria outlined in Sect. 2.3. While IC measurements were available for all 30 hydrologic events, ~~not all fewer~~ events had the required 5 sample points for all of the cations analyzed by sufficient ICP-MS measurements (i.e., ~~for~~ boron, barium, iron, manganese, chromium, strontium, and copper), ~~because concentrations of these elements were often very low.~~ Furthermore, some events had to be excluded from

250 further analysis for individual solutes due to high relative standard errors of cQ slopes and/or intercepts (see Sect. 2.5). This
resulted in ~~Between 24 to and 30 usable events were available~~ for major ions measured with the IC. More than 20 events were
evaluated for all other solutes, except manganese and copper. The concentrations of these two solutes were low and variable,
resulting in no clear power-law relationship with discharge for many events. Consequently, ~~but~~ only data from 17 and 11
events were usable for manganese and copper, respectively. ~~analyzable for copper and 17 for manganese. All other solutes
yielded analyzable data for more than 20 events.~~

We quantified most environmental controls for all 30 events. However, meaningful event-water contributions could only be
calculated for 22 events from stable water isotope measurements. Ratios of precipitation concentration to the pre-event
baseflow solute concentration were not available for all events and all solutes due to sporadic problems with the rain collector.
260 Also, these ratios were not assessed for EC, because EC was not measured in precipitation. Table 1 provides an overview of
the range of environmental controls covered by the selected events. Some small events lasted only a few hours, whereas other
events were extended, multi-day storms, and antecedent wetness conditions ranged from relatively dry to very wet. Although
all events took place between May and November, they spanned a wide range of air temperatures and weather conditions.

265 3.2 Characterization of solute contributions from different source areas

Streamwater concentrations at Erlenbach were dominated by calcium, sulfate, magnesium, and sodium, with median
concentrations between 2 and 48 mg L⁻¹ (Table 2). Conversely, median streamwater concentrations of manganese and copper
were low at around 1 µg L⁻¹, and concentrations of chromium were even lower. All other solutes (strontium, barium, boron,
chloride, potassium, nitrate, and iron) were observed at intermediate concentrations in the Erlenbach streamwater.

270 We can group different solutes based on their most important sources in the Erlenbach catchment as determined from their
concentration ranges in groundwater, streamwater, and precipitation, as well as output-input flux indices (Table 2). The
concentrations of calcium, strontium, barium, and boron in the groundwater samples were similar to, or higher than, those in
streamwater. Concentrations of magnesium, sodium, and sulfate were higher in streamwater than in the groundwater samples,
275 suggesting that other, unsampled, groundwaters with higher concentrations also contribute to streamflow. In general,
gGroundwater concentrations of weathering products are likely to be highly heterogeneous due to spatially variable
contributions from the geochemically complex Flysch bedrock (Fischer et al., 2015; Kiewiet et al., 2019). Precipitation
concentrations of ~~these~~ weathering products are low, and flux indices close to 1, implying that they are primarily derived from
within-catchment processes (Table 2). In this paper, we will refer to these solutes as groundwater-sourced.

280 The output-input flux index of chloride at Erlenbach was 0.33 for the snow-free periods, but was -0.13 if calculated from daily
data over the two full years (not shown here), suggesting that precipitation is the most important source of chloride in the

Erlenbach catchment on an annual basis (Zobrist, 2010). Chloride is likely to be relatively unreactive in the Erlenbach catchment.

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Nitrate concentrations in Erlenbach streamwater can also be mainly attributed to atmospheric inputs as well as manure inputs from grazing. The output-input flux index of nitrate was -0.52 (even without taking manure inputs into account), indicating that nitrate was either taken up into vegetation or possibly volatilized as ammonia (i.e., the catchment acted as solute sink). Potassium is supplied to the stream through weathering of the bedrock, with some atmospheric inputs, which contribute more to streamflow fluxes of potassium than those of calcium or magnesium. Potassium is also known to be retained in the soils and cycled internally in forest stands (Hornung et al., 1986; Likens et al., 1994).

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Iron was the most abundant trace metal in the Erlenbach streamwater, with median concentrations of around $5 \mu\text{g L}^{-1}$. Streamwater iron concentrations were substantially higher than the concentrations measured in groundwater or precipitation, and very high in the soil water of the neighboring and geologically similar Studibach catchment, pointing toward the soil layer as predominant source of streamwater iron (Table 2). Groundwater concentrations of manganese at Erlenbach were broadly similar to those measured in streamwater, but soil water concentrations (and also groundwater concentrations; not shown here) in the Studibach catchment were substantially higher. This indicates that manganese may be sourced both from groundwater and soil water. The storage of iron and manganese in and release from soil layers are likely controlled by the complexation of these trace metals with organic material (Bloomfield, 1953; Harter and Naidu, 1995), and the strong redox-sensitivity of these elements (Drever, 1988; Basu et al., 2010; Koger et al., 2018). The concentrations of the trace metals chromium and copper were low in all analyzed compartments, and a distinct source cannot decisively be identified. In the neighboring Studibach catchment, Kiewiet et al. (2019) observed the highest concentrations of chromium at predominantly dry sites, and highest concentrations of iron and manganese at predominantly wet sites. These observations suggest that concentrations of trace metals are probably not homogeneously distributed in the Erlenbach catchment.

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3.3 High inter-event variability that differs from the ~~long-term~~two-year behavior

We calculated ~~long-term~~two-year cQ relationships based on the snow-free recession periods of the 2-year time series, and event-scale cQ behavior from the recessions of the 30 extracted events. ~~Long-term~~Two-year cQ relationships were relatively narrow and well-defined for most solutes (Fig. 2), resulting in low uncertainties of ~~long-term~~two-year slopes and intercepts (Table S1). Furthermore, ~~long-term~~two-year slopes and intercepts calculated for the whole time series were broadly similar to those determined from only hydrograph recession periods (Table S1), largely because recessions comprised nearly all of the ~~long-term~~two-year data. Thus our analysis can straightforwardly compare cQ behavior during individual recessions with the ~~long-term~~two-year cQ behavior across two years of recessions.

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Figure 2 shows that major ions and EC exhibited dilution behavior (slopes < 0 ; lower concentrations at higher discharges) across the ~~long-term~~two-year record, but with different degrees of variability. The data clouds in the cQ space were more scattered for e.g. chloride, potassium, and nitrate compared to those of e.g. calcium, magnesium, and sodium. Iron, manganese, and chromium showed a mobilization behavior (~~long-term~~two-year slope > 0 ; higher concentrations at higher discharges), while the ~~long-term~~two-year cQ relationship of copper indicated chemostasis (slopes ≈ 0).

Event-scale cQ relationships at Erlenbach were much more variable than the ~~long-term~~two-year behavior. A comparison between different events revealed substantial inter-event variability in both slopes and intercepts for a number of solutes (colored lines in Fig. 2 and blue circles in Fig. 3). The extent of this variability differed dramatically among the solutes. Individual events followed the ~~long-term~~two-year trend for calcium, magnesium, sodium, strontium, and EC, for example, whereas they deviated substantially from the ~~long-term~~two-year trend for potassium, chloride, and nitrate.

For most solutes, the averages of all event-scale intercepts (light-blue diamonds in Fig. 3a) were similar to the ~~long-term~~two-year intercepts (red bars in Fig. 3a), because discharge was normalized by its mean value (see Sect. 2.5). The inter-event variability in intercept values was particularly high for chloride, nitrate, and some of the trace metals, possibly suggesting changes in sources, flowpaths or reaction rates of these constituents between events.

Conversely, the slopes of the event-scale cQ relationships differed substantially from the ~~long-term~~two-year behavior for some of the elements (Figs. 2 and 3). This was true in particular for three solutes with significant atmospheric inputs (chloride, potassium, and nitrate), which exhibited dilution behavior on the ~~long-term~~two-year (~~long-term~~two-year slope < 0), while their cQ slopes of individual events varied between dilution (event slope < 0) and mobilization (event slope > 0).

None of the solutes exhibited stronger dilution behavior, on average, during events (blue diamonds in Fig. 3b) than over the long term (red bars in Fig. 3b). In the case of potassium, chloride, nitrate, and manganese, most individual events (blue circles in Fig. 3b) exhibited substantially weaker dilution, or greater mobilization, than the ~~long-term~~two-year cQ relationship (red bars in Fig. 3b). Considered together, these results indicate that dilution processes were equally important, or more important, over the long term than during individual events.

Solute with similar sources and similar chemical properties tend to exhibit similar ~~long-term~~two-year cQ behavior and similar degrees of inter-event variability in slopes and intercepts. For example, calcium, magnesium, sodium, strontium, barium, boron, sulfate, and EC all exhibited well-defined ~~long-term~~two-year dilution behavior and little variability in both cQ slopes and intercepts at the event scale. All solutes exhibiting this behavior were previously identified as groundwater-sourced in the Erlenbach catchment (Sect. 3.2). Average event slopes of these solutes were approximated well by the ~~long-term~~two-year behavior (Fig. 3b), resulting in event patterns that fan out around the high-discharge section of the ~~long-term~~two-year cQ trend

350 (Fig. 2). This similarity between ~~long-term~~two-year and event-scale behavior indicates that similar mechanisms controlled solute and water mobilization both during individual events and over the long term for these solutes.

Conversely, potassium, chloride, and nitrate have substantial atmospheric inputs at Erlenbach. These three solutes were characterized by ~~long-term~~two-year dilution behavior, and high variability in event slopes ranging from negative to positive
355 values, along with some inter-event variability in intercept values. These solutes exhibit event cQ patterns that fan out and stack up around the ~~long-term~~two-year relationship. This large inter-event variability in cQ slopes may plausibly arise from varying degrees of atmospheric deposition, evapotranspiration, and dry deposition, resulting in temporally and spatially variable concentrations of chloride, potassium, and nitrate in shallow soil layers. A large variability in soil water concentrations was indeed observed in the neighboring Studibach catchment (Table 2). In the case of nitrate and potassium, the inter-event
360 variability may also be affected by biological uptake and reaction processes. In summary, chloride, nitrate, and potassium showed a much more diverse behavior on the event-scale and also – at least to some extent – on longer timescales than the purely groundwater-sourced solutes.

The trace metals iron, manganese, and chromium were mobilized during events, as reflected in positive event and ~~long-~~
365 ~~term~~two-year cQ slopes. Interestingly, this mobilization behavior was more pronounced (i.e. slopes were steeper) on the event scale than on longer timescales. In contrast to the other metals, copper concentrations in streamwater suggested chemostatic behavior over long timescales, whereas some mobilization behavior was evident on the event scale (Fig. 2). These findings suggest that the trace metals were mainly sourced from the soil layers, and the observed cQ behavior of manganese and iron confirms common assumptions about them being co-located in the soil layers where they are bound to organic material or
370 present as oxides.

The grouping of solutes based on cQ behavior aligns well with the previously identified source areas in the Erlenbach catchment (Sect. 3.2). These alignments were most obvious for the purely groundwater-sourced solutes, because they could be clearly attributed to one main source. For most other solutes, the combination of different sources and the co-occurrence of
375 reaction and mixing processes resulted in less clear patterns. A scatterplot of event slopes against event-intercept values (Fig. 4) supports the grouping of solutes and illustrates the different degrees of inter-event variability. The low uncertainty of the calculated slopes and intercepts furthermore confirms that the observed variability among events is real-world behavior rather than noise.

380 Other likely modulators of the variability observed for different solutes are their ionic form and their possible occurrence as nanoparticulates. Cations are known to undergo exchange buffering through electrostatic binding to negatively charged sites in soils (Helling et al., 1964; Rhoades, 1982). This likely resulted in less variable cQ behavior on the event scale for the cationic solutes calcium, magnesium, sodium, strontium, and barium compared to the anionic solutes sulfate and boron. These anions

are less buffered by ion exchange and showed a far more variable cQ behavior. Two other anions, chloride and nitrate, also exhibited highly variable cQ behavior at the event scale. It consequently seems likely that exchange buffering processes modulate the degree of observed inter-event variability. Nevertheless, the importance of cation exchange buffering on the variability of solute behavior cannot be well constrained with our data set, because most analyzed cations are groundwater-sourced species while two of the three solutes with substantial atmospheric inputs, chloride and nitrate, are anions. The only cation with important atmospheric input (potassium) is biologically very active, potentially obscuring the effects of cation exchange buffering. With respect to the trace metals, a large part of their total concentration can occur as natural nanoparticulates (Gottselig et al., 2017), which may undergo different transport and adsorption processes compared to their dissolved forms. This likely had a strong effect on their cQ behavior at Erlenbach.

3.4 Environmental controls of the observed inter-event variability in cQ relationships

We used weighted rank correlation coefficients to assess how variations in cQ slopes and intercepts from event to event were related to seasonality indicators, relative input concentrations, antecedent wetness conditions, event characteristics, and event-water contributions. A heatmap (Fig. 5) illustrates how event-scale cQ slopes and intercepts depended on these different environmental controls. Individual examples of these relationships are shown in Fig. [S1-S2](#) for different solutes and drivers.

The event-scale cQ intercepts for all solutes, regardless of their dominant source, generally responded similarly to each control (with the exception of chloride; Fig. 5a). Seasonality indicators and antecedent wetness conditions were the most important environmental controls on cQ intercepts for all solutes, with drier and warmer conditions resulting in higher concentrations in streamwater. By contrast, although the effects of each control on event-scale cQ slopes were broadly similar within groups of solutes that shared the same dominant source (precipitation, soil water, and groundwater), they often differed between these groups (Fig. 5b). In the following, we therefore discuss the behavior of the event-scale cQ slopes of these groups of solutes together, rather than discussing individual solutes.

We found that the event-scale cQ slopes of groundwater-sourced solutes were positively correlated with seasonality indicators, with weaker solute dilution (i.e., less negative cQ slopes) during warmer conditions. Antecedent wetness conditions and event characteristics were other important factors controlling the event-scale cQ behavior of most groundwater-sourced solutes. We found stronger dilution (i.e., more negative cQ slopes) during larger events associated with wetter antecedent conditions. cQ slopes were also more negative when event-water contributions were larger, consistent with stronger dilution of groundwater-sourced solutes by larger volumes of recent rainfall (i.e., event water). Most of the observed relationships were less clear for boron (which is primarily sourced from groundwater, but does not occur as a cation, but instead as either undissociated boric acid or as the borate anion, depending on pH), supporting the hypothesis that differences in ionic charge modulate event-scale cQ behavior. By contrast, however, sulfate (an anion) showed very similar dependencies as the cations in groundwater,

contradicting this hypothesis. Streamwater electrical conductivity (EC) at Erlenbach is dominated by the two most abundant solutes, calcium and magnesium (along with their counter-ion, bicarbonate), which are groundwater-sourced. Consequently, the event-scale cQ behavior of EC depends on similar factors as that of the groundwater-sourced solutes.

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For the solutes with significant atmospheric inputs (chloride, potassium, and nitrate), the effects of possible environmental controls on cQ slopes were less clear, but still indicated similar behavior among the solutes of this group. We found that the event-scale cQ slopes of chloride and nitrate were influenced by antecedent wetness conditions, with dilution behavior during wetter conditions and mobilization behavior during drier conditions (Fig. 5b). This can potentially be explained by stronger evapo-concentration of these solutes in the soil under drier conditions. We also observed a tendency toward more positive slopes with higher relative input concentrations for all three solutes, and during events in which the event-water contribution was larger. The observed dependencies of nitrate and potassium differed somewhat from those of chloride, likely due to the overprinting with reaction processes acting on these solutes, and due to overlapping patterns from atmospheric and groundwater sources in the case of potassium.

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Among the trace metals, iron often exhibited contrasting behavior compared to the others (Fig. 5b). While manganese, chromium, and copper showed a tendency toward stronger mobilization under colder and wetter conditions, iron tended to be mobilized more during warmer and drier conditions. Given that both iron and manganese are found predominantly in wetter soils (in the neighboring Studibach catchment; Kiewiet et al., 2019), we would have expected these two metals to depend on similar drivers. However, Kiewiet et al. (2019) also observed higher concentrations of manganese in riparian areas compared to iron. We would expect these riparian zones to be activated first during a rain event, whereas soils farther from the stream would likely only start to contribute to streamflow later. This sequence of contributions from source areas dominated by different trace metals could potentially explain why the cQ slopes of the trace metals varied differently with seasonality, event characteristics, and event-water contributions. The high concentrations of manganese in riparian areas may also explain the very high cQ slopes observed for this element. As the relative contribution from riparian areas decreases later in the recession, manganese concentrations in streamwater drop rapidly, decreasing more-than-proportionally compared to discharge. [As metal complexation and mobilization is known to depend on various factors such as pH and redox conditions in the soil layer \(Gotoh and Patrick, 1972, 1974\), further field measurements are necessary to better understand the mobilization of trace metals from soil layers during hydrologic events.](#)

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4 A classification scheme for cQ relationships in the Erlenbach catchment

Previous studies have shown that hydrological controls on streamwater chemistry are mostly invariant on time scales of weeks to months; for example, Gwenzi et al. (2017) found similar cQ behavior for weekly to monthly sampling frequencies, and Godsey et al. (2019) found similar cQ behavior in weekly/monthly grab samples and in year-to-year variations in annual

450 average concentrations. Other studies have also shown that long-term average cQ behavior is relatively independent of the
sampling frequency (e.g., Bieroza et al., 2018). Our analysis of event-scale cQ patterns, as defined by high-frequency sampling
within and between individual events, provides a new perspective on cQ relationships. Our results indicate that solute responses
to discharge variations can be fundamentally different during individual events compared to longer time scales. These
differences in cQ behavior reveal the effects of the dominant sources, reaction processes, and ionic forms of the different
455 solutes.

Figure 6 provides an overview of the different cQ patterns observed at Erlenbach, and the role of various environmental
controls in shaping these patterns during events and over the long term. For groundwater-sourced solutes such as calcium,
magnesium, and sodium, we found that ~~long-term~~two-year cQ relationships were relatively good approximations of event-
460 scale cQ patterns. These solutes exhibited little inter-event variability, and their cQ relationships on both the event scale and
longer time scales were dominated by dilution. The inter-event variability of cQ slopes of groundwater-sourced solutes was
mainly controlled by season, event size, and event water contributions.

Atmospherically derived solutes also exhibited ~~long-term~~two-year dilution behavior, but their event-scale behavior ranged
465 from dilution to mobilization, with event-scale cQ patterns stacking up and fanning out around the ~~long-term~~two-year cQ
relationship (Figs. 2 and 6). Their event-scale cQ slopes were usually more positive than their ~~long-term~~two-year cQ slopes,
indicating a stronger importance of chemostatic and mobilization mechanisms on the event scale. The controls on event-scale
cQ slopes were less clear for nitrate and potassium than for chloride, likely due to reaction processes (in the case of potassium
and nitrate) or overprinting of contributions from different sources (in the case of potassium). Nevertheless, we observed
470 stronger mobilization following drier antecedent conditions and during events with larger event-water contributions,
suggesting that evapo-concentration of atmospherically deposited solutes plays an important role.

Trace metals showed mixed behavior in our analysis, likely due to different patterns of distribution in soils and groundwaters,
and possibly also due to their presence as nanoparticulates (Fig. 6). In our study, the different trace metals often responded
475 differently to environmental controls, possibly reflecting differences in their relative abundance in the riparian zone, in their
complexation mechanisms, in their redox sensitivities, and in their biological cycling (Herndon et al., 2015; Koger et al., 2018).

5 Summary and conclusions

Our analysis of 30 events extracted from a 2-year time series of sub-hourly streamwater solute measurements demonstrated
480 that concentration-discharge (cQ) relationships at the hydrologic event scale can differ substantially from those over the long
term. In addition, cQ relationships varied greatly from event to event for some solutes (e.g., potassium, chloride, and nitrate),

but varied much less for others (e.g., calcium, magnesium, sodium, and EC). The variability in cQ relationships among different hydrologic events (and solutes) could be linked to a range of environmental controls.

485 Our analysis would not have been possible if we had analyzed only a few solutes or collected data only during a handful of hydrologic events, as is common practice in catchment hydrochemistry studies (Rode et al., 2016). To understand the complex mechanisms governing solute storage and release from different parts of the catchment, it is necessary to analyze many different solutes, and to sample multiple hydrologic events at high enough frequency to capture event behavior. However, we are aware that sampling and analysis systems like the one that we employed at Erlenbach are resource-intensive, and thus
490 difficult to deploy in many field situations. Our analysis suggests, however, that a viable alternative may be to analyze one solute (or proxy thereof) from every major store and streamwater source in the catchment. For instance, EC in Erlenbach streamwater exhibited very similar cQ relationships as calcium, magnesium, and sodium, making it a suitable tracer for groundwater-sourced solutes (in other catchments, EC may be a better proxy for solutes from other compartments; Benettin and Van Breukelen, 2017). Automated sensors for nitrate and phosphorous are available and can provide high-frequency
495 information on biogeochemically active solutes. The analysis of trace metals is not available through automated sensors, but in many cases DOC can be a suitable proxy for iron and some other trace metals (Nierop et al., 2002; Grybos et al., 2007). [pH measurements may also provide helpful insights into the mobilization of trace metals from soil layers.](#) All in all, with sufficient knowledge about the possible sources that contribute to streamflow in a catchment, much simpler measurement systems may still provide meaningful insight into solute storage and release processes.

500

The grouping of solutes based on their dominant source, cQ behavior, ionic character, and dependence on environmental controls is illustrated in a schematic overview in Fig. 6. This overview highlights similarities and differences among solutes, summarizes their expected range of cQ behavior on the event scale, and indicates their sensitivities to environmental controls. Analyses of event-scale cQ patterns may help in identifying the vulnerability of different catchment compartments to changes
505 in land use and climate, and may benefit monitoring and management strategies. For example, if the climate warms and summers become drier in this area of Switzerland, our data suggest that the event slopes of chloride, nitrate, and potassium will become more positive, leading to enhanced flushing of these solutes during hydrologic events. Evaluating the generality of the results presented here will require further studies in catchments of contrasting climate, geology, and land use.

510 **Data availability**

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

Author contribution

JLAK and JWK conceptualized the study. JLAK, JF, and BS collected and analyzed the solute data and LK the soil moisture
515 data from Studibach, JLAK analyzed the data set, and JLAK prepared the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no competing interests.

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Table 1: We assessed 15 environmental controls grouped into five different categories: seasonality indicators, relative input concentrations, antecedent wetness conditions, event characteristics, and event-water contributions. Minimum and maximum values indicate the ranges observed in the dataset. Relative input concentrations are specific for every solute (and not available for all solutes and events), whereas all other controls do not differ between individual solutes. Event-water contributions were only assessed for 22 out of 30 events. Groundwater levels are expressed as negative values so that the maximum corresponds to the wettest conditions, consistent with the other wetness indicators.

| Variable | Description | Min. value | Max. value |
|--------------------------------|---|--------------------------------------|--|
| Seasonality indicators: | | <i>cold ↔ warm</i> | |
| T_{event} | Average air temperature during the event (°C) | -0. 31 <u>37</u> | 15. 67 <u>56</u> |
| T_{24h} | Average air temperature in the 24h before the event (°C) | 6.23 | 18. 45 <u>62</u> |
| SW | Proximity to midyear (-) | 0.31 | 1.000 <u>.99</u> |
| Relative input concentrations: | | <i>low ↔ high</i> | |
| c_P/c_{Q_0} | Ratio between solute concentrations in precipitation and baseflow (solute-specific) (-) | 8.62 <u>.0</u> e-4 | 40.963 <u>.91</u> |
| Antecedent wetness conditions: | | <i>dry ↔ wet</i> | |
| GW_{ini} | Initial groundwater level (cm) | -76. 59 <u>70</u> | -9.70 |
| AP_{7d} | Amount of precipitation in the 7 days before the event (mm) | 4.800 <u>.00</u> | 112111 <u>.40</u> <u>70</u> |
| Q_{ini} | Baseflow before the onset of the event (mm h ⁻¹) | 7.7e-04 | 0. 11 <u>10</u> |
| Event characteristics: | | <i>small ↔ large</i> | |
| $P_{intensity}$ | Maximum precipitation within 4h (mm) | 7.10 | 27.70 |
| Q_{tot} | Total amount of event discharge (mm) | 0. 82 <u>90</u> | 28. 48 <u>86</u> |
| P_{tot} | Total amount of precipitation (mm) | 8.00 | 6768 <u>.7060</u> |
| Q_{tot}/P_{tot} | Runoff coefficient | 0.06 | 0. 47 <u>45</u> |
| ΔQ | Max. discharge change (L s ⁻¹) | 24.82 <u>23.80</u> | 901.45 <u>680</u> <u>.60</u> |
| Δt_{event} | Event duration (days) | 0. 52 <u>48</u> | 4. 69 <u>77</u> |
| Event-water contributions: | | <i>pre-event water ↔ event-water</i> | |
| Q_e/P | Event water in streamflow as fractions of precipitation (event runoff coefficient) (-) | 4.96 <u>.3</u> e-03 | 0. 17 <u>16</u> |
| Q_e/Q | Event water in streamflow as fractions of discharge (-) | 0.04 | 0. 46 <u>43</u> |

650 **Table 2: Median solute concentrations and their upper/lower quartiles in streamwater, groundwater, and precipitation in the Erlenbach catchment and in soil water in the adjacent Studibach catchment. Groundwater solute data were collected at one to three**
different sampling times at two pumping wells located in the upper part of the catchment. These are probably not representative of
groundwater concentrations throughout the catchment, but still provide a rough indication of which solutes dominate groundwater.
Concentrations in precipitation and streamwater were obtained from the time series recorded at the Erlenbach outlet, excluding
months with snow. *N* indicates the number of samples the calculations are based on. EC was not analyzed in precipitation or soil
655 **water. Concentrations greater than 10 $\mu\text{g L}^{-1}$ are rounded to the nearest integer. Flux index calculations (see Eq. (1)) of the snow-**
free season are based on the same period as the analyzed time series and consequently do not represent long-term fluxes. Positive
flux indices quantify the fraction of the output flux that was generated in the catchment, while negative flux indices quantify the
fraction of the input flux retained in the catchment. A value of 0 is obtained if input and output fluxes balance. The ratio of
precipitation to streamflow water fluxes during the snow-free period was 1.75 (compared to a ratio of 1.41 for the time from January
1st 2017 to December 31st 2018).

| Solute | Streamwater concentration [solutes: $\mu\text{g L}^{-1}$, EC: $\mu\text{S cm}^{-1}$] ($N=1916-4930$, $N_{\text{EC}} =$ 99576) | Groundwater concentration [solutes: $\mu\text{g L}^{-1}$, EC: $\mu\text{S cm}^{-1}$] ($N=2-6$) | Precipitation concentration [$\mu\text{g L}^{-1}$] ($N=817-975$) | Flux indices of the snow- free period [-] | Soil water concentration at Studibach [$\mu\text{g L}^{-1}$] ($N=41-102$) |
|-----------------|--|--|---|---|---|
| EC | 264 [222-292] | 389 [354-398] | n.a. | n.a. | n.a. |
| Ca | 47891 [40528-52835] | 50057 [46648-53880] | 1366 [948-1896] | 0.93 | 13553 [3461-31007] |
| Mg | 3076 [2494-3498] | 1767 [1503-2013] | 79 [59-112] | 0.93 | 13588 [3885-20429] |
| Na | 2338 [1711-2924] | 1590 [1220-1936] | 126 [91-226] | 0.74 | 781 [526-999] |
| Sr | 299 [230-347] | 556 [551-560] | 4.25 [2.9-6.4] | 0.95 | 99 [0.77-297] |
| Ba | 46 [34-55] | 61 [57-65] | 0.91 [0.65-1.47] | 0.91 | 36340 [9675-61548] |
| B | 8.5 [6.7-11] | 21[6.4-39] | 0.60 [0.31-1.22] | 0.70 | 12 [8.3-20] |
| SO ₄ | 9157 [6542-14102] | 4944 [3557-6531] | 172 [64-472] | 0.92 | 892 [428-1865] |
| K | 805 [659-907] | 1197 [1101-1210] | 81 [39-208] | 0.13 | 527 [273-879] |
| Cl | 264 [183-370] | 891 [768-961] | 33 [14-75] | 0.33 | 739 [447-1319] |
| NO ₃ | 527 [384-758] | 1672 [514-1840] | 368 [158-812] | -0.52 | 84 [9.5-565] |
| Fe | 4.6 [2.3-15] | 1.21 [0.61-2.07] | 1.40 [0.87-2.46] | 0.87 | 18 [6.6-109] |
| Mn | 0.18 [0.11-0.54] | 0.42 [0.25-1.8] | 0.21 [0.09-0.61] | 0.54 | 12 [4.0 -64] |
| Cr | 0.05 [0.04-0.07] | 0.13 [0.13-0.14] | 0.01 [0.01-0.03] | 0.62 | 0.47 [0.02-1.04] |
| Cu | 1.22 [0.98-1.45] | 0.28 [0.24-0.56] | 0.21 [0.09-0.46] | 0.41 | 2.68 [1.84-4.83] |

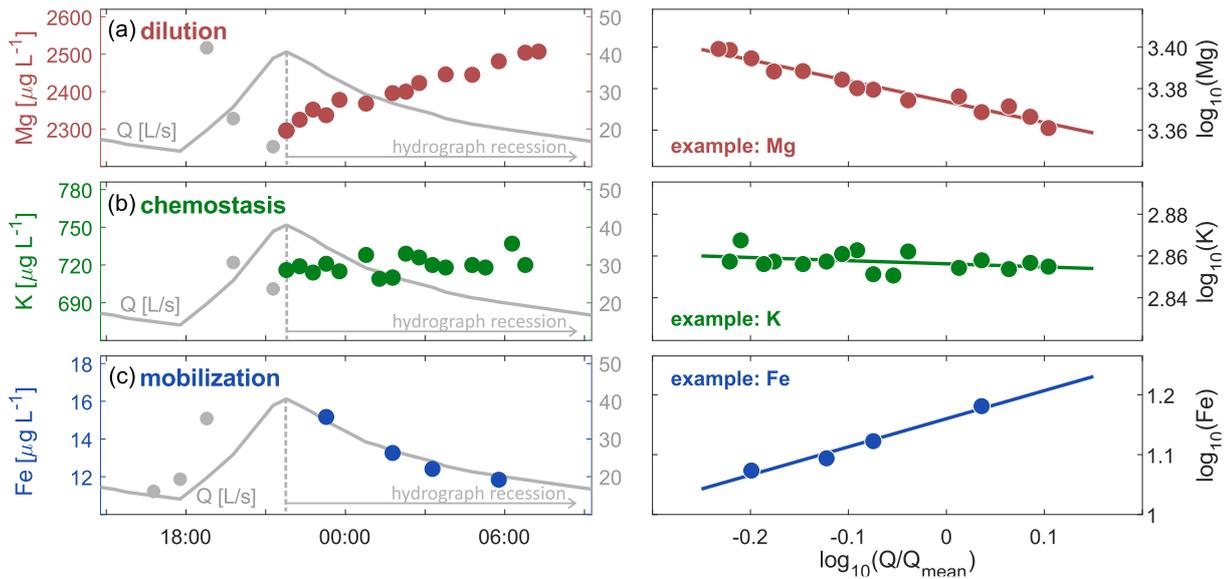
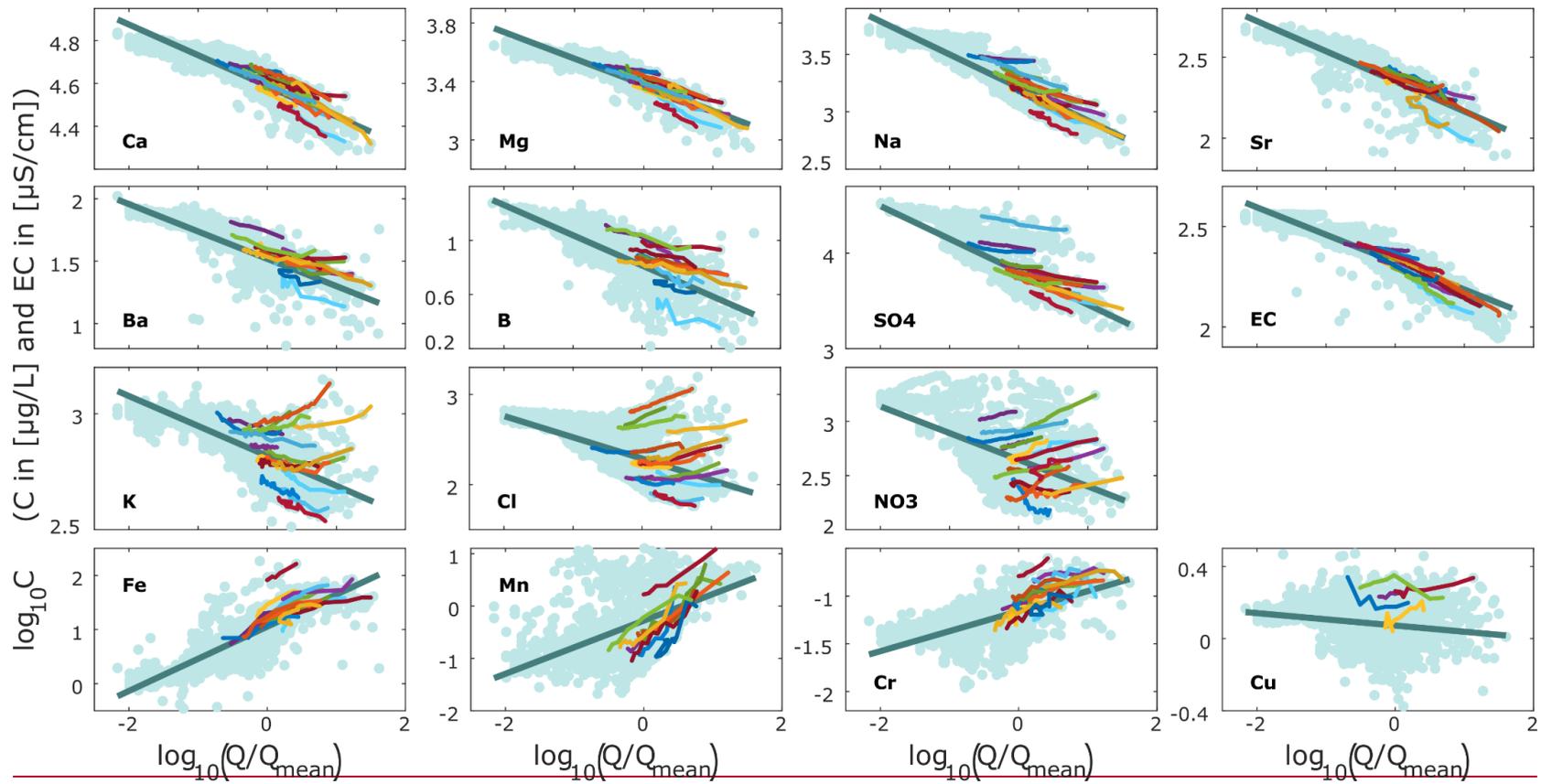
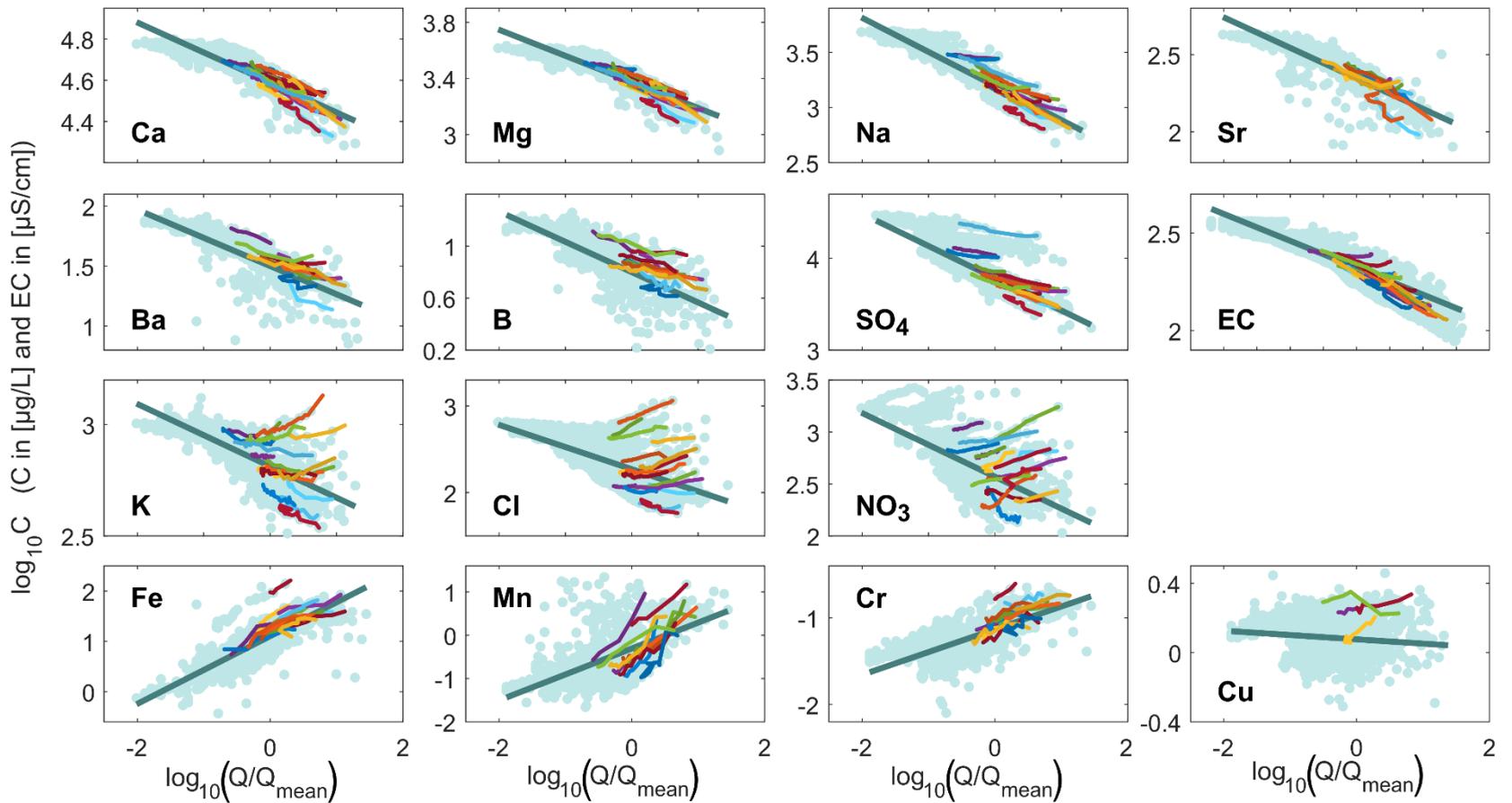


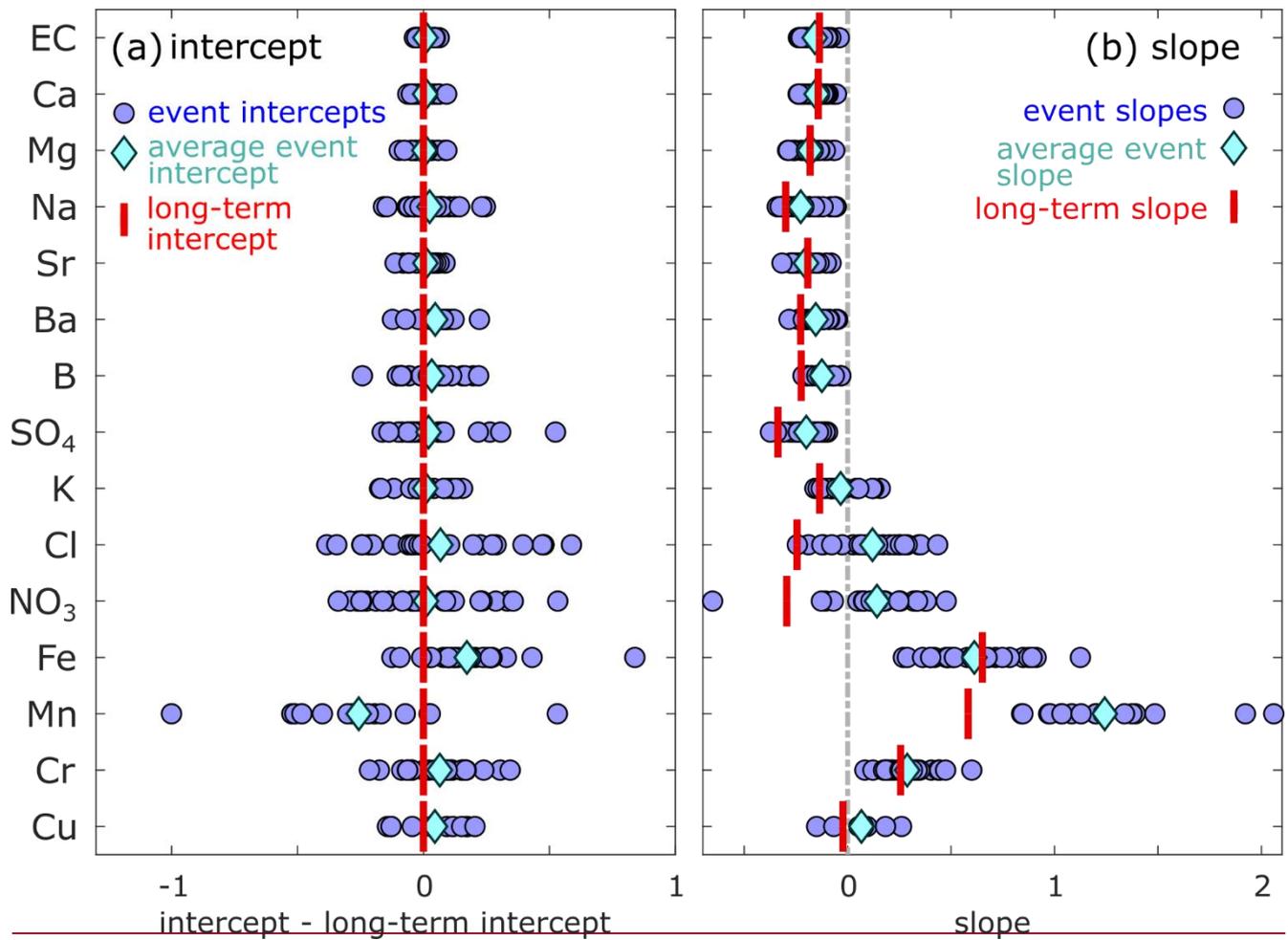
Figure 1: Time series of discharge and solute concentrations (left panels), and corresponding cQ relationships (right panels) for a single recession, illustrating dilution behavior (Mg, top panels), chemostatic behavior (K, middle panels), and mobilization behavior (Fe, bottom panels). Solute with negative cQ slopes (dilution, a) will have their lowest concentrations at high flows, and thus will exhibit increasing concentrations during hydrograph recession. Because this concentration increase is usually less-than-proportional to the decrease in discharge, power-law cQ slopes are rarely steeper than -1. Solute with cQ slopes near zero (chemostatic, b) do not vary systematically with discharge. Solute with positive cQ slopes (mobilization, c) exhibit higher concentrations at high flows, and decreasing concentrations during hydrograph recession. Power-law cQ slopes steeper than 1 indicate that concentrations change more-than-proportionally to discharge.

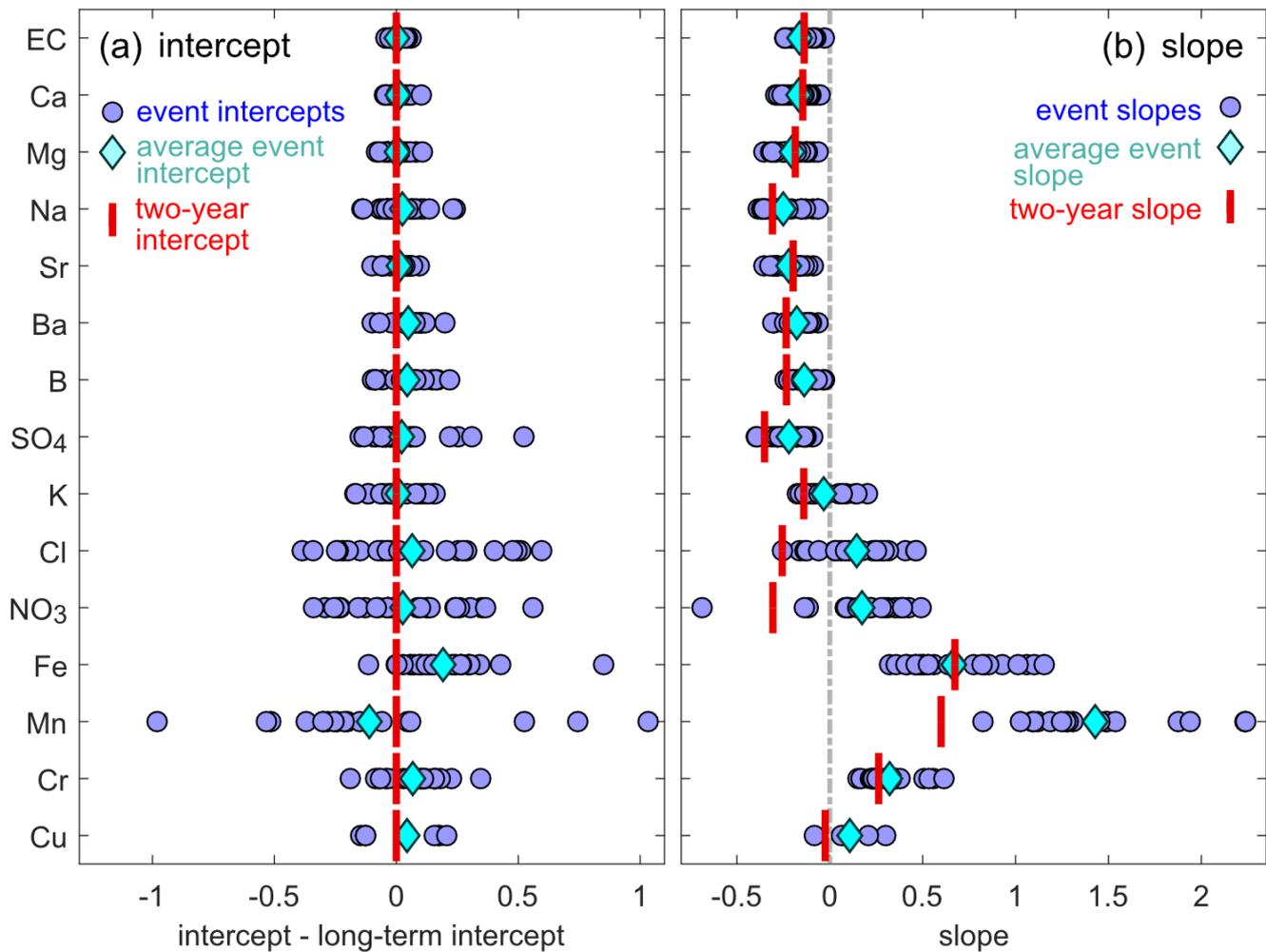




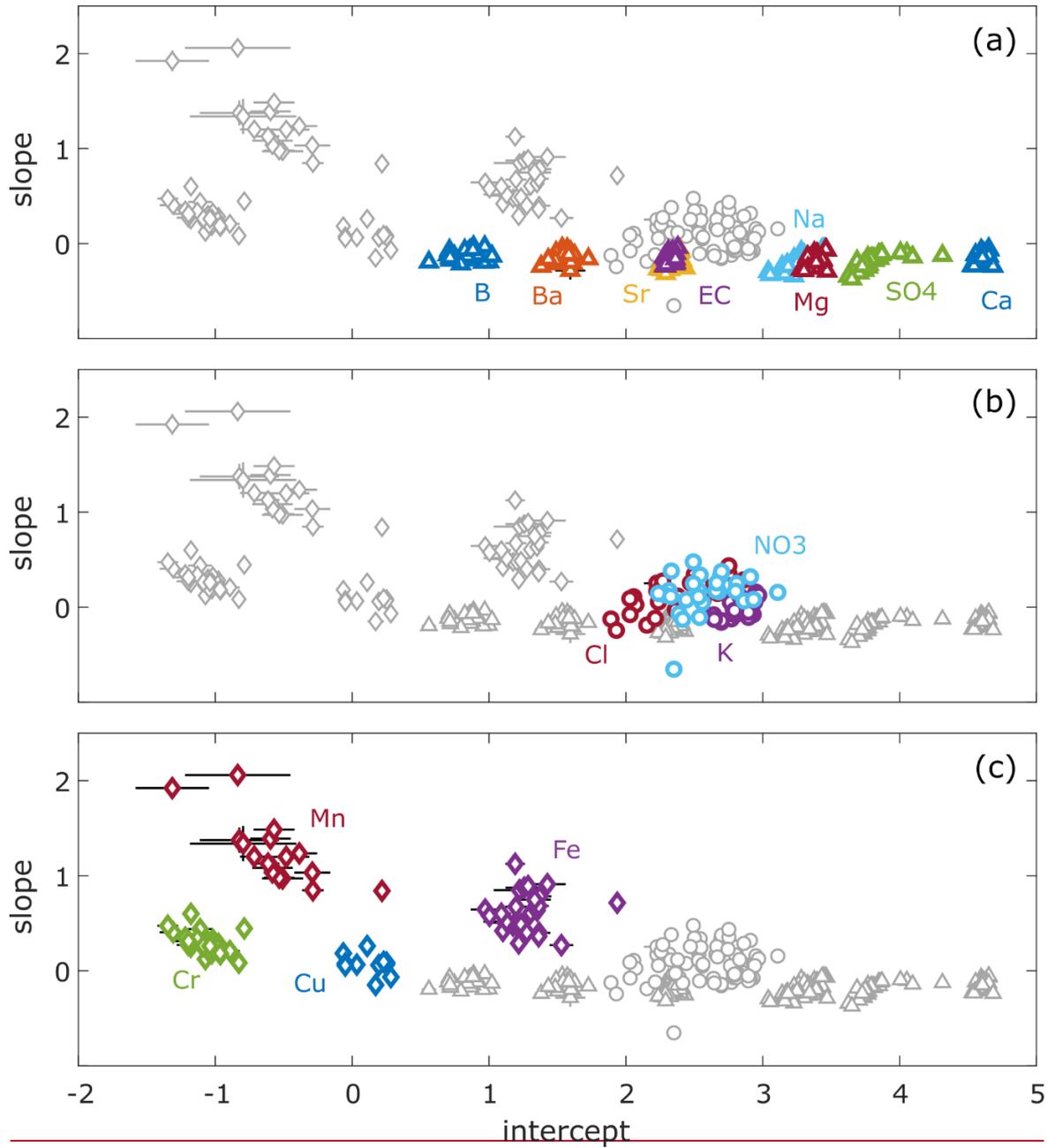
675 **Figure 2: Long-term Two-year cQ relationships** from the entire recession time series (data points are shown in light blue and the dark blue line indicates the power-law fit), compared to the cQ behavior of individual events (colored lines; up to 20 events are shown for better visibility). Discharge is normalized by the average discharge of the time series. Most solutes exhibit a **long-term two-year dilution pattern**, whereas the trace metals iron, manganese, and chromium exhibit a **long-term two-year mobilization pattern**. The cQ relationships vary much more from event to event for some solutes (e.g. potassium, chloride, and nitrate) than for others (e.g. calcium, magnesium, sodium, and EC).

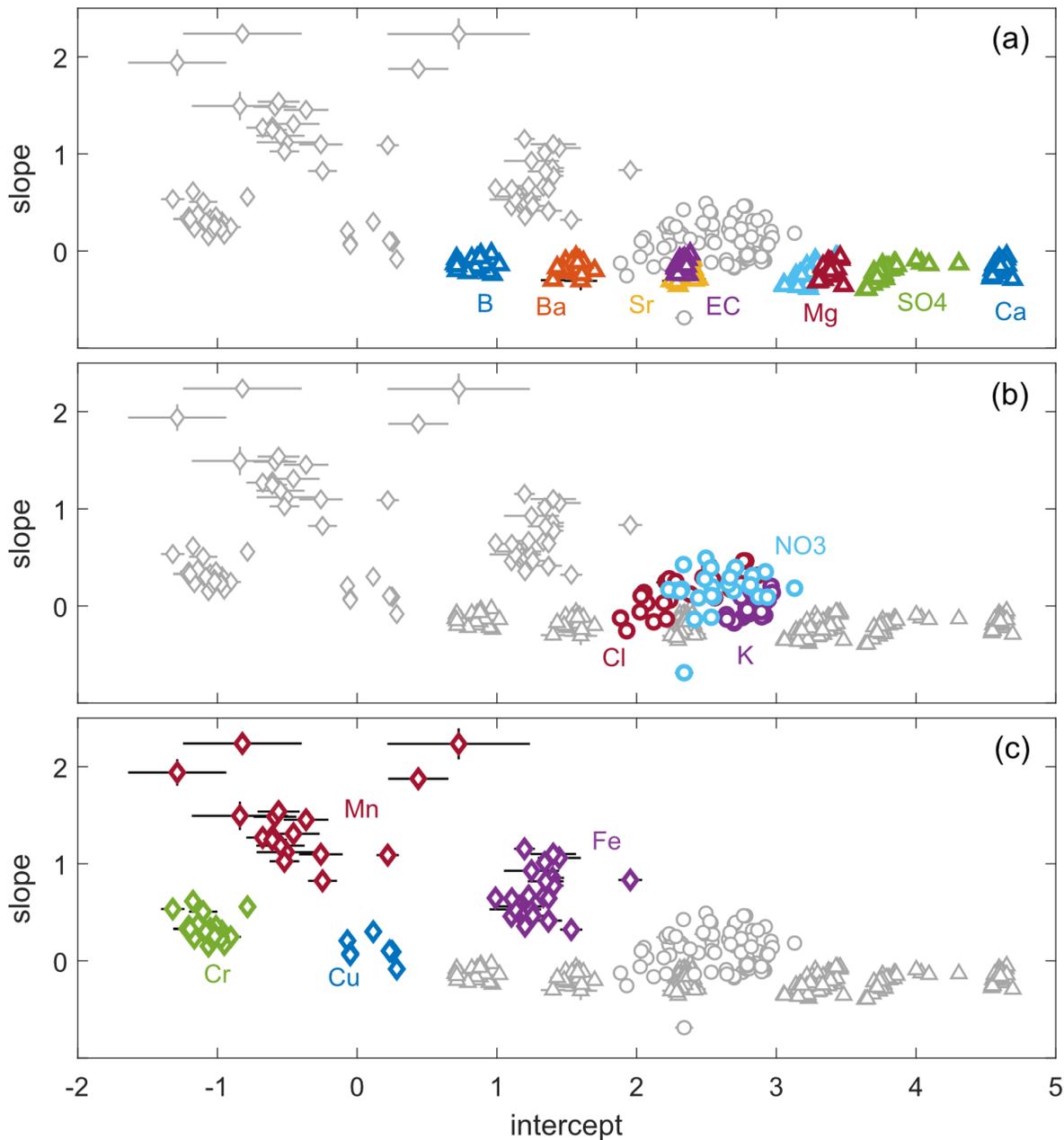
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685 Figure 3: A comparison of event-scale and long-term two-year cQ intercepts (a) and slopes (b). Blue circles represent intercepts and
 slopes for individual events, light-blue diamonds represent the averages of all events, and red bars indicate the slopes and intercepts
 of the long-term two-year cQ relationships. If the red bar is close to the light-blue diamond, the long-term two-year slope or intercept
 value is a good approximation of the average event slope or intercept. In panel (a), event cQ intercepts are expressed relative to the
long-term two-year average for better visual comparison of the solutes. Event-scale intercepts and slopes vary substantially for
 690 solutes in the lower half of the figure (from chloride to chromium), but vary little for most groundwater-sourced solutes. Because
 we normalized discharge by the mean discharge value, long-term two-year intercepts approximate the average event-intercepts.
Long-term Two-year slopes also approximate the event slopes for most groundwater-sourced solutes, but long-term two-year slopes
 are more negative than event slopes for, e.g., chloride, nitrate, and manganese.



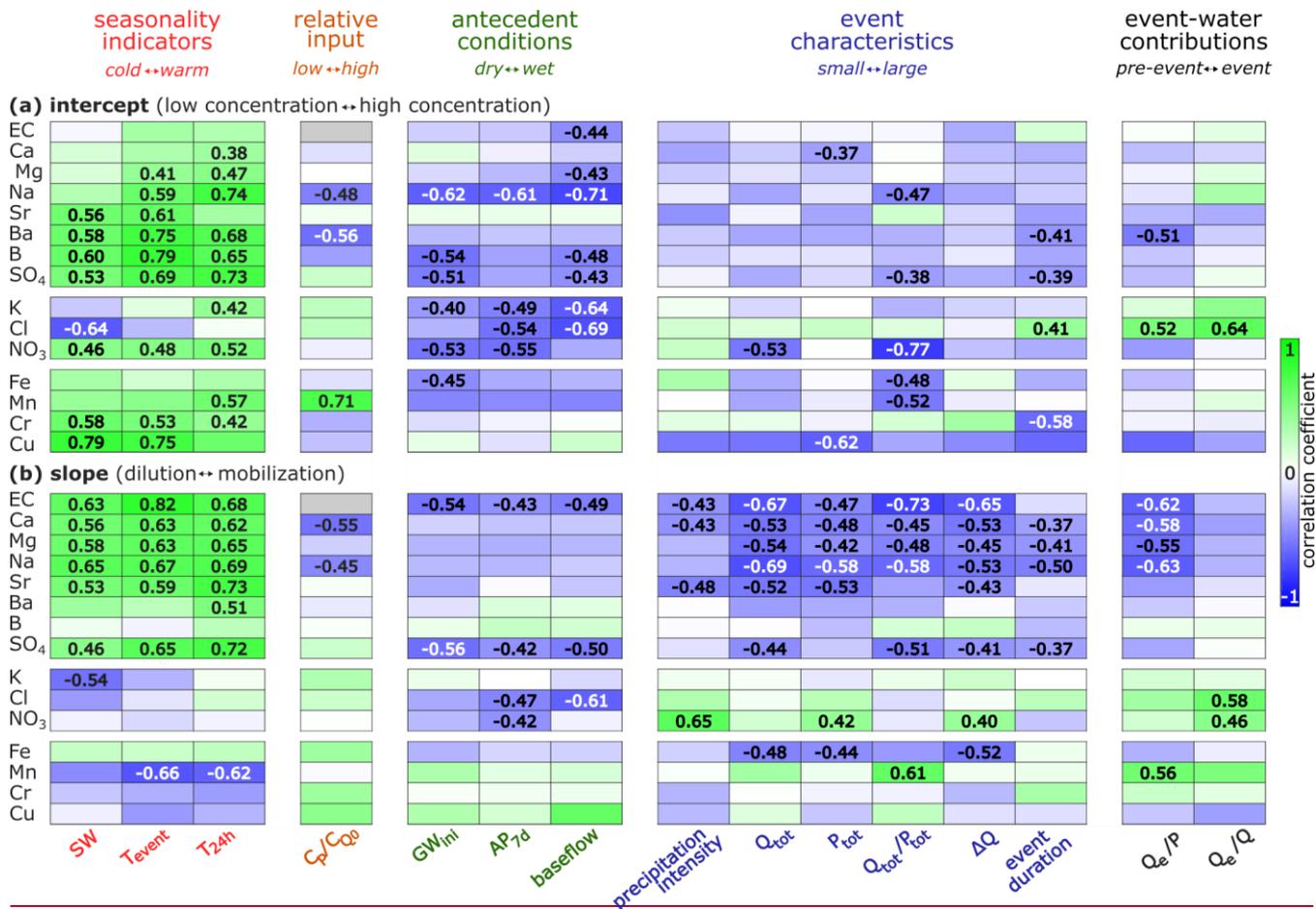


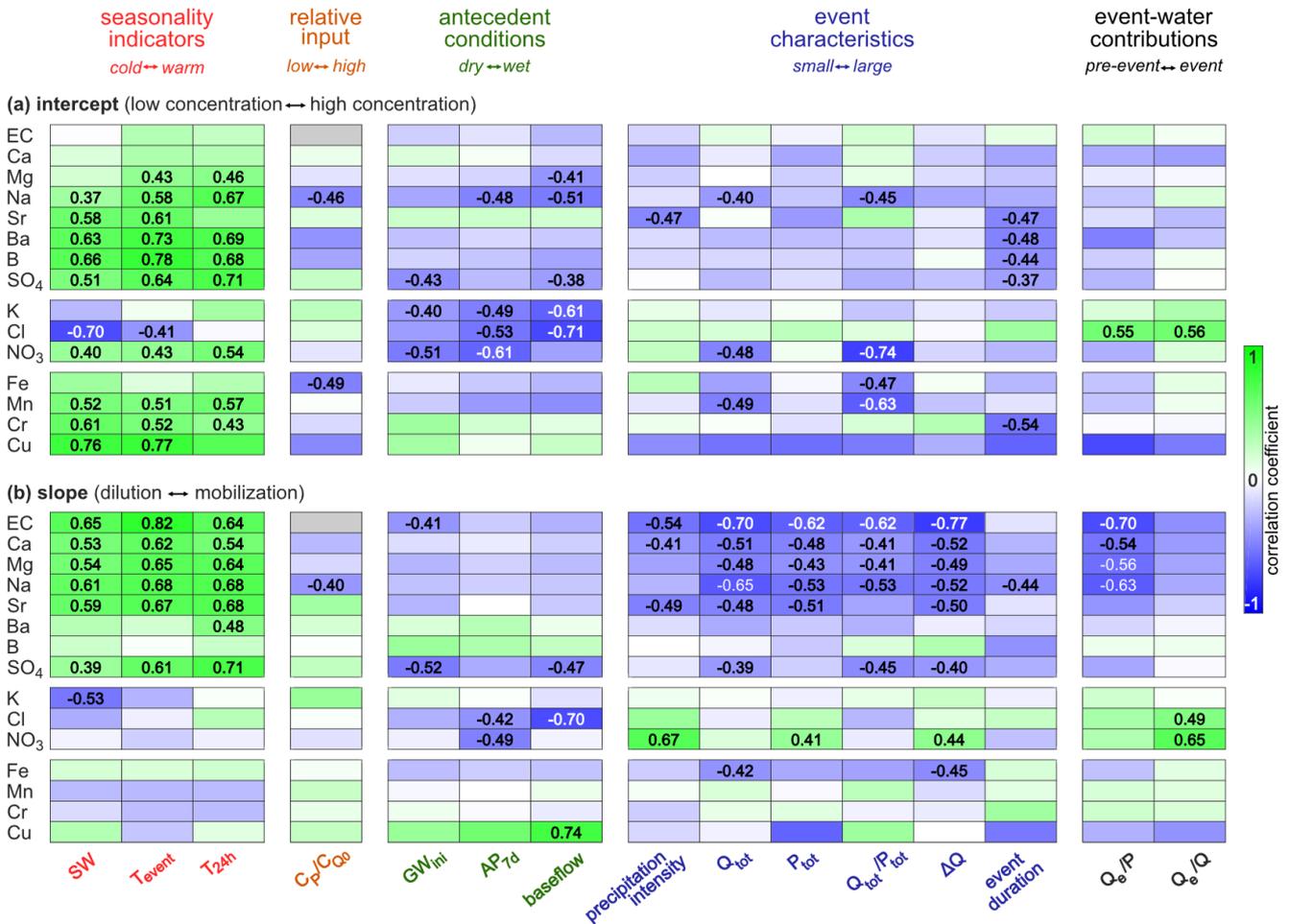
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Figure 4: Scatter plots of event cQ slopes and intercepts of the 14 different solutes and EC (error bars indicate one standard error). Solutes from different dominant sources cluster and exhibit similar ranges of variability. (a) Groundwater-sourced solutes cluster closely around similar slopes and show little inter-event variability in both slopes and intercepts. (b) Intercepts and slopes of solutes with significant atmospheric input (i.e., chloride, nitrate, and potassium) vary substantially among events. (c) The slopes of trace metals are generally higher than those of the other solutes (indicating predominantly mobilization behavior), and are also highly variable among events. The uncertainty in the estimated slopes and intercepts is mostly smaller than the variability **between-among** events, indicating that the observed inter-event variability in slopes and intercepts reflects real-world behavior rather than sampling and measurement noise. **To corroborate this, a version of the same figure including all cQ slopes and intercepts even from events**

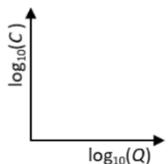
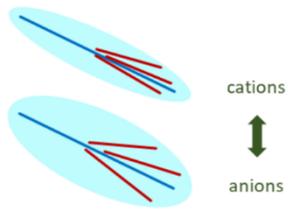
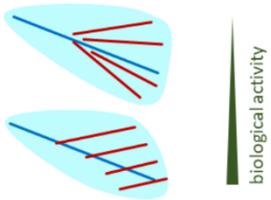
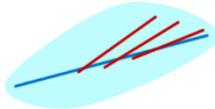
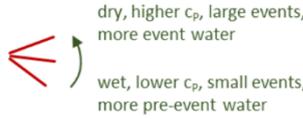
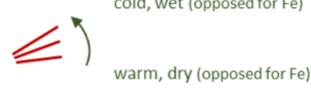
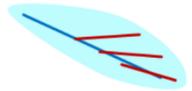
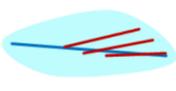
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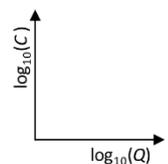
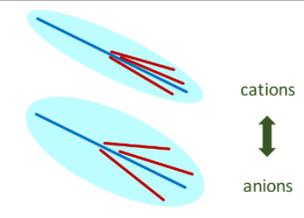
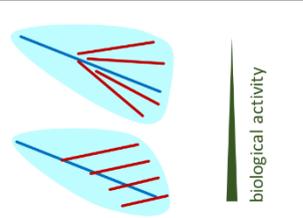
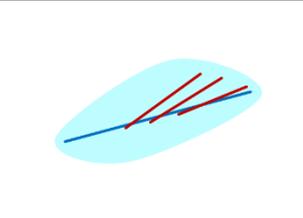
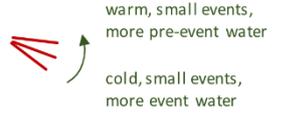
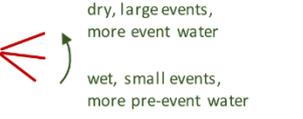
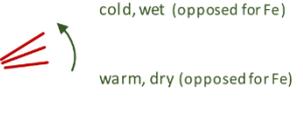
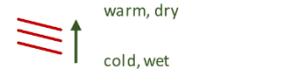
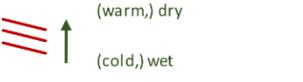
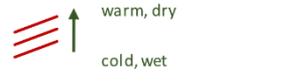
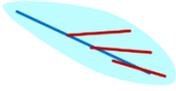
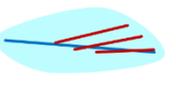
excluded from further analysis due to high relative standard errors in slope and/or intercept values is provided in the supplemental material.





710 Figure 5: Weighted rank correlation coefficients expressing the dependence of event-scale cQ intercepts (a) and slopes (b) on
 715 different environmental controls (seasonality indicators, relative input concentrations, antecedent wetness conditions, event
 characteristics, importance of event-water contributions). Green fields indicate positive rank correlations, blue fields indicate
 negative correlations, and darker colors indicate stronger relationships. Only statistically significant ($p < 0.05$) correlation coefficients
 are displayed. Gray fields for EC indicate relationships that could not be assessed because EC was not measured in precipitation.
 For solutes featuring dilution patterns, e.g. calcium in panel (b), positive correlations indicate relationships that become more
 chemostatic when the controlling variable increases. For solutes with mobilization patterns, e.g. iron in panel (b), positive
 correlations indicate enhanced mobilization when the controlling variable increases. For meanings of abbreviations, please refer to
 Table 1.

| dominant source | GROUNDWATER | PRECIPITATION | SOIL |
|--|---|---|---|
| <p>cQ-behavior</p>  |  |  |  |
| <p>solute mobilization (cQ slope):</p> <p><i>long term</i></p> <p><i>event scale</i></p> | <p>slope < 0</p> <p>slope < 0</p> | <p>slope < 0</p> <p>-1 < slope < 1</p> | <p>slope > 0</p> <p>slope > 0</p> |
| <p>variability in cQ space:</p> <p><i>long term</i></p> <p><i>event scale</i></p> | <p>well-confined</p> <p>low variability</p> | <p>high scatter</p> <p>high variability</p> | <p>high scatter</p> <p>some variability</p> |
| <p>potential modulators of event-scale behavior</p> | <p><i>ionic form:</i></p> <p>lower variability for cations due to exchange buffering</p> | <p><i>biological activity:</i></p> <p>increases the variability</p> | <p>presence as <i>nanoparticulates:</i></p> <p>likely affects the solute mobilization during events</p> |
| <p>drivers & controls of inter-event variability:</p> <p><i>slope</i></p> |  <p>seasonality indicators & event characteristics</p> |  <p>antecedent conditions & event-water contributions</p> |  <p>seasonality indicators & antecedent conditions</p> |
| <p>drivers & controls of inter-event variability:</p> <p><i>intercept</i></p> |  <p>seasonality indicators & antecedent conditions</p> |  <p>(seasonality indicators &) antecedent conditions</p> |  <p>seasonality indicators & antecedent conditions</p> |
| <p>solutes (at Erlenbach)</p> | <p>Ca, Mg, Na, Sr, Ba, B, SO₄, EC</p> | <p>Cl, NO₃</p> | <p>Fe, Mn, Cr</p> |
| <p>mixed behavior</p> |  <p>long-term cQ scatter and inter-event variability increases with contribution from precipitation, e.g. K.</p> |  <p>long-term behavior becomes more chemostatic with increasing contributions from precipitation, mobilization behavior on the event scale.</p> | |

| dominant source | GROUNDWATER | PRECIPITATION | SOIL |
|--|---|---|---|
| cQ-behavior  |  |  |  |
| solute mobilization (cQ slope): <i>long-term</i> <i>event-scale</i> | slope < 0 slope < 0 | slope < 0 -1 < slope < 1 | slope > 0 slope > 0 |
| variability in cQ space: <i>long-term</i> <i>event-scale</i> | well-confined low variability | high scatter high variability | high scatter some variability |
| potential modulators of event-scale behavior | <i>ionic form:</i> lower variability for cations due to exchange buffering | <i>biological activity:</i> increases the variability | presence as <i>nanoparticulates:</i> likely affects the solute mobilization during events |
| drivers & controls of inter-event variability: <i>slope</i> |  <p>seasonality indicators & event characteristics</p> |  <p>antecedent conditions & event-water contributions</p> |  <p>seasonality indicators & antecedent conditions</p> |
| drivers & controls of inter-event variability: <i>intercept</i> |  <p>seasonality indicators & antecedent conditions</p> |  <p>(seasonality indicators &) antecedent conditions</p> |  <p>seasonality indicators & antecedent conditions</p> |
| solutes (at Erlenbach) | Ca, Mg, Na, Sr, Ba, B, SO ₄ , EC | Cl, NO ₃ | Fe, Mn, Cr |
| mixed behavior |  <p>long-term cQ scatter and inter-event variability increases with contribution from precipitation, e.g. K.</p> |  <p>long-term behavior becomes more chemostatic with increasing contributions from precipitation, mobilization behavior on the event scale.</p> | |

720 **Figure 6: Schematic overview of cQ behavior based on dominant solute sources and environmental controls at the Erlenbach catchment. Solute originating from similar sources generally behave similarly, and their cQ patterns are mostly sensitive to the same environmental controls. The light-blue patches in cQ behavior show the expected variability in the long-term cQ data, with average long-term cQ relationships indicated by the blue lines. Red lines show cQ relationships for individual events and indicate the degree of inter-event variability.**