Response to the interactive comment of Anonymous Referee #2 on

“Concentration-discharge relationships vary among hydrological events, reflecting differences in event characteristics” by Julia L. A. Knapp et al.

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,…”

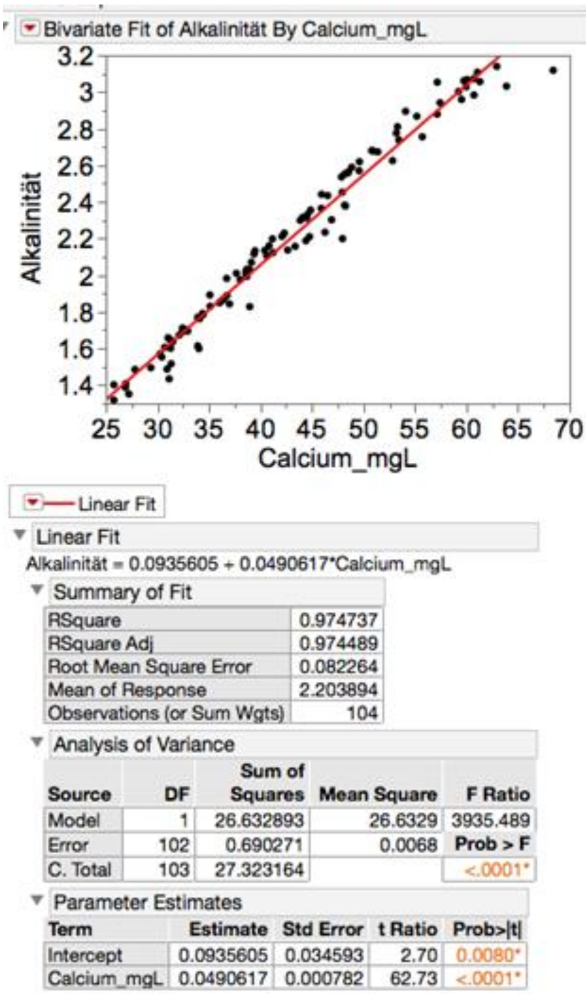
2. Section 2.2. Dataset: I miss information on some essential parameters like silica, alkalinity, and pH:
a. Was silica measured by ICP-MS but below detection? That seems surprising. Or was it not measured, or perhaps not feasible with ICP-MS? Because silica is usually a very useful element in cQ studies.

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 (Zobrist, 2010). <u>Groundwater chemistry is thus dominated by calcium, magnesium, and their counter-anion, bicarbonate</u>.”



Linear Fit

Alkalinität = 0.0935605 + 0.0490617*Calcium_mgL

Summary of Fit

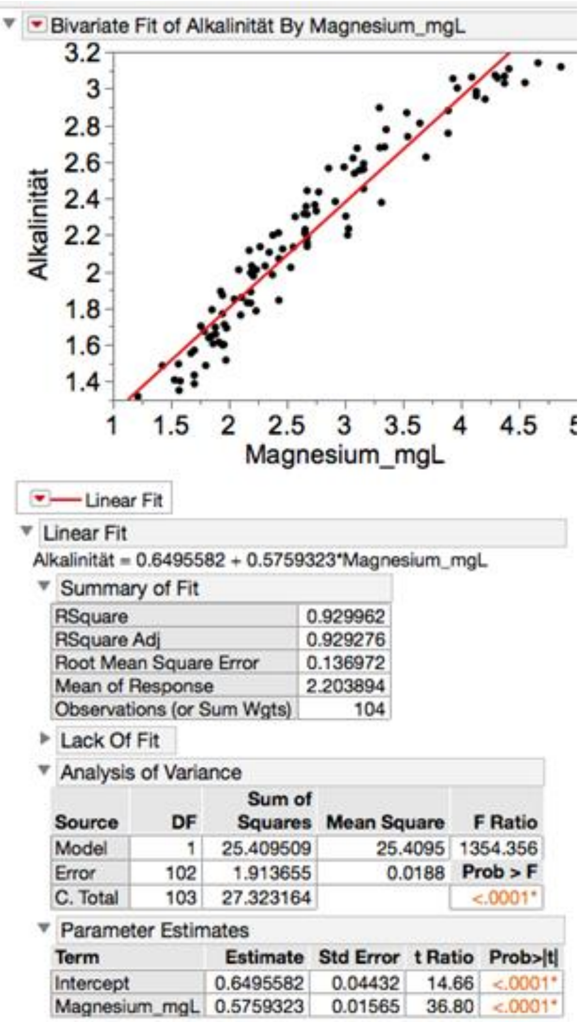
RSquare	0.974737
RSquare Adj	0.974489
Root Mean Square Error	0.082264
Mean of Response	2.203894
Observations (or Sum Wgts)	104

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	26.632893	26.6329	3935.489
Error	102	0.690271	0.0068	Prob > F
C. Total	103	27.323164		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.0935605	0.034593	2.70	0.0080*
Calcium_mgL	0.0490617	0.000782	62.73	<.0001*



Linear Fit

Alkalinität = 0.6495582 + 0.5759323*Magnesium_mgL

Summary of Fit

RSquare	0.929962
RSquare Adj	0.929276
Root Mean Square Error	0.136972
Mean of Response	2.203894
Observations (or Sum Wgts)	104

Lack Of Fit

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	25.409509	25.4095	1354.356
Error	102	1.913655	0.0188	Prob > F
C. Total	103	27.323164		<.0001*

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.6495582	0.04432	14.66	<.0001*
Magnesium_mgL	0.5759323	0.01565	36.80	<.0001*

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 (lines 475-481, 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."

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 for individual solutes due to high relative standard errors of cQ slopes and/or intercepts (see Section 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, for which only data from 17 and 11 events were usable, respectively."

4. Section 3.2. Line 269: Clarify which solutes precisely are meant with "these so-lutes" 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 (Fischer et al., 2015; Kiewiet et al., 2019). Precipitation concentrations of ~~these~~ weathering products are low,…"

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,…."

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."

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."

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)

References:

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.

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.