Hydrology and
Earth System
Sciences
Discussions

Interactive comment on "Concentration-discharge relationships vary among hydrological events, reflecting differences in event characteristics" *by* Julia L. A. Knapp et al.

Anonymous Referee #2

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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.

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.

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.

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).

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.

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?

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?

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?

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

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?

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.

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