

Interactive comment on “A lab in the field: high-frequency analysis of water quality and stable isotopes in streamwater and precipitation” by Jana von Freyberg et al.

Anonymous Referee #2

Received and published: 19 December 2016

General comment: In their work ‘A lab in the field: High frequency analysis of water quality and stable isotopes in streamwater and precipitation’ von Freyberg et al. present the set up and proof-of-concept of a new automatic sampling system for high-resolution measurements of stable water isotopes and stream solutes. The analytical components mainly consist of a laser spectroscopy system for stable water isotope analysis and an ion chromatograph for the measurement of anions and cations. Both instruments are joined by a sophisticated peripheral set up. Particular emphasis has been put into the reduction of carry over effects during operation when switching between the two water sources sampled.

The paper is clearly structured and easy to read. The system’s set up is impressive

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and the authors made great effort with a proof-of-concept. The precision achieved for both systems is excellent. I recommend to accept the paper for publication. However, I see some aspects of their set up that should be acknowledged in a revised version:

(1) The idea of a lab in the field is nice, but in fact the system requires a proper housing and full power connection. The system is far from being mobile and field deployable. To my understanding it is still a lab in a house (which is located in vicinity to a catchment).

(2) Automatic wet chemistry instrument set ups are routinely operated by water provisioning services (e.g. in sewage treatment works) and by larger state environmental agencies or research facilities for surface water monitoring. Such systems are expensive (and therefore hardly used in basic research projects), but in place. See reviews from Gray et al. 2006, *Environmental Chemistry*, <http://dx.doi.org/10.1071/EN05059> or Bende-Michl and Hairsine 2010, *Journal of Environmental Monitoring*, DOI: 10.1039/B910156J.

(3) Even though the authors achieved a reasonable high sampling frequency of 30 min this set up does not allow to capture the potentially very high temporal change of stable water isotopes in precipitation. This short term variation (that is missed by aggregating to 30 min composite samples or by sampling only the last precipitation sequence of a 30 min period) might be responsible for some of the differences found for the chemical- and isotope-based hydrograph separations. For high temporal resolution application see results in Pangle et al. 2013, already cited in the paper, or Moerman et al. 2013, *Earth and Planetary Science Letters*, <http://dx.doi.org/10.1016/j.epsl.2013.03.014>. I do not fully understand why the two sampling systems for isotope and chemical compositions are not operated independently, but parallel. In a synchronized, parallel set up, the systems could sample stable water isotopes independently in the order of minutes utilizing the full power of the continuous water sampler while (composite or grab) samples for the ion chromatograph are sampled in 30 min resolution.

(4) The current set up is limited to two water sources. Given the set up and limita-

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tion of 30 min sampling frequency the system is only partly extendable with regard to sampling additional sources such as groundwater, tributaries or nearby standing water bodies. The sampling of additional sources, however, is needed to partially resolve the differences in the various hydrograph separations outlined in Chapter 5.

Specific comments.

L16: Missing space between value and unit, check throughout the manuscript

L47 ‘much longer much smaller’ – I do not get what you intend to say.

L48-52 There are two new papers out by Aubert and Breuer 2016, PLoS ONE, doi:10.1371/journal.pone.0153138 and Aubert et al. 2016, Scientific Reports, DOI: 10.1038/srep31536, that explicitly show the value of high resolution measurements of nitrate, might be worth considering here (or at least to have a look at).

L101 You sampled an internal standard every 3 h (see Line 280). So why did you not use these standards to correct absolute isotope values?

L246 An installation in a hut with power supply is not an installation in the field as the title of the paper indicates. At least not to my understanding of a field deployable system. I suggest to revise the title.

L257 I do not agree that the correlation of daily precipitation is good and therefore allows to derive subdaily precipitation patterns. We know how variable precipitation can be in space. As almost 20% of the variance of daily sums cannot be explained by the correlation, I can only speculate on the potential differences in hourly or even higher frequency precipitation rates. For future application of the system, I strongly suggest to add an independent met station to the field lab, which is negligible in costs compared to all the other instruments and peripherals used to set up this lab.

L264 Is there any reason to use a large bucket of 10 L rather than a substantially smaller container to sample from? Or utilize an even larger container to produce composite rather than grab samples. Chapter 5 As the paper is mainly a description of the

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technical set up, I wonder a bit on the extensive evaluation of the event/pre-event water contribution in this chapter. While I see this a very interesting aspect of the utilization of the system in a fully operational application, I think this section can be reduced for this more technical paper. In fact, the discussed potentially missing end member to better understand the observations (groundwater, soil water, spatially variable precipitation) reflects the limitation of the current set up where only two water sources can be sampled in high temporal resolution (see also general comment, bullet point (4)).

L423-483 The difference of the isotope and chemical tracer derived hydrograph separation are enormous. The dissimilarity of results is so large, that the overall applicability of the approach seems to be questionable. As the authors stress, it goes beyond the scope of this paper to resolve the issue and further end members need to be identified to explain the observations. Thus, the discussion remains at least partly speculative. The current set up of the system does not allow to sample more sources in high resolution. To this end, the system described in the paper is limited to investigate more simple mixing processes of two end members, rather than complex mixing processes typical for catchments. Part of the observation might be due to the non-conservativeness of the chemical tracers. At least for NO₃⁻ I doubt its feasibility to be used as a real tracer, particularly in highly biological reactive top soils. Another potential explanation is variable source areas and their connectivity to the stream, with source areas being switched on/off during events.

L444 revise expression: moisture cannot be mineralized

Chapter 5.4 This section misses a real discussion. There are at least a few papers that look into the effect of sampling frequency on hydrograph separation or mean transit time estimation that could be discussed here. Stockinger et al. 2014, <http://dx.doi.org/10.1016/j.jhydrol.2016.08.007>; Timbe et al. 2015 doi:10.5194/hess-19-1153-2015; Birkel et al. 2012 DOI: 10.1002/hyp.8210; Inamdar et al. 2013 DOI: 10.1002/wrcr.20158.

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L514 I do not agree that you can conclude from Fig 3 that a 3 h sampling frequency would be sufficient. May be you can conclude this from Fig 11. However, in L516 you note yourself that even intervals of 3 h can results in a significant loss of information.

L566 Despite the technical achievement and the effect of the high frequency sampling, the authors could stress even more the highly uncertain results of their hydrograph separation (even though this should not be the major focus of the paper). Combining the results of Fig 9 and Fig 11 I conclude that whatever model you have, it could easily be verified by an 'appropriate' selection of solutes and their sampling frequency, as the uncertainty to derive a 'true' hydrograph separation is very large.

Chapter 6 (or elsewhere in the discussion). After I read the conclusions, I wonder why the authors have decided to include an ion chromatography system that limits really high resolution measurements and therefore also limits sampling further water sources. At least for some of the solutes measured, ion selective probes or UV hyperspectral photometry sensors (reviewed by Rode et al. and already included in the paper) could be used as an alternative analytical system with substantially lower costs as well.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., doi:10.5194/hess-2016-585, 2016.

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