

# ***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.***

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General comment: This paper describes the development and performance of an advanced high-frequency analyser of both water isotopes and major ions in stream flow and precipitation. The authors provide a thorough account of the instrument design and operation and an assessment of analytical performance. The integration of the many components represents a significant engineering effort. The instrumentations analytical data quality is impressive, in particular the precision of isotope analysis. The instrumentation is described as a ‘lab in the field’ and high quality data can certainly be produced in real time during extended deployments. However, I question whether it can be described as a true field instrument considering its limited portability, multi

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component complexity (Fig. 1) and relatively high requirements for power and shelter. The field deployment described was in an outbuilding of the research institute, presumably with mains power but it is unclear what environmental conditions the instrument was exposed to (e.g. range of temperature fluctuations). A photograph of the actual setup used would be a useful addition. The last 1/3 of the paper (Section 5 - comparison of event water fractions) is concerned with the interpretation of the month long field trial. This section seems somewhat too long given that the main aim of the paper (as per the introduction) is the description of the development and field trial of the instrument (these are adequately described through sections 1-4). Moreover, the interpretation provided in section 5 is somewhat hampered by lack of data on important potential contributions to stream flow (soil and groundwater) as only two endmembers (base flow and precipitation) are considered. This limitation is clearly acknowledged by the authors. A substantial shortening of section 5 should be considered, although a shortened comparison of event-water fractions based on isotopes and ions should be retained as it provides a very good demonstration of the value of high frequency isotope measurement compared to the more traditional use of solute tracers in discrete samples taken at longer intervals. The manuscript is clearly written and the conclusions are sound and well supported by the data presented.

Specific comments: 2. Methodology: For the laboratory based tests the analysis system was not calibrated as only relative isotope values were required - however, it is not clear if full calibration to the VSMOW scale or only drift correction was performed in the field tests – please expand on this (P 8 L280). Figures 5 and 6 display actual field data, e.g. in Fig. 5 data is shown relative to GMWL and LMWL so this comparison would require that full calibration was performed. One of the limitations / uncertainties in the calculation of event-water fractions is (as stated by the authors) the precise definition of end member compositions. As the isotope composition (O and H) is often regarded as the most reliable tracer of event water it could be argued that the highest possibly frequency of isotope measurement of both stream and precipitation water should be prioritised. In this regard it seems illogical that the measurement of

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isotope compositions was limited to 30 min intervals in order to synchronise data with the IC measurements which required this amount of time. This is particularly the case when a continuous water isotope instrument was used, wouldn't it be more beneficial to fully utilise its capability to perform truly continuous analysis, especially for precipitation which can vary significantly over much shorter time intervals than 30 min? At 30 min intervals, a 'conventional' CRDS instrument with a sequential injection/evaporation cycle could equally well have been used (apart from possible maintenance requirements). A similar auto sampling system was used for the IC and presumably this required regular maintenance.

3.1 Optimisation of sample injection. . . The explanation provided for the delta dependence on hydraulic head difference (P 5 L 152 and Fig. 2) may not be the full explanation. The Picarro CWS uses a high air flow rate (possibly  $\approx 500$  mL/min as I recall) and this has the effect that the vapour generated is not in isotopic equilibrium with the liquid water flowing inside the ePTFE tube. The vapour is significantly depleted in d18O and d2H compared to equilibrium values due to the faster diffusion through the membrane of the light isotopologues compared to the heavy. This effect does not matter much as long as air and water flows and temperatures are kept constant for both sampling and calibration standards. However, the large fractionation effect probably tends to make the system prone to artefacts such as an altered pump rate. The use of a relatively cheap peristaltic water pump as opposed to the CWS supplied diaphragm pump would provide improved flow and lift characteristics (as does the expensive Dosimo pumps used in this study). P 6 L 213. Drift is attributed to biofilm growth, was this growth assumed or actually observed? Possibly temperature drift (inlet air and water) was also a factor in the field deployment? Was the instrumentation exposed to outdoor temperature fluctuations or was temperature regulated indoors? P 6 L 217. How constant was the memory effect? If relatively constant, a data correction could be applied. Presumably it would be a function of analysis time (washout effect)

4. Application in the field: P 9 L 323. It is unclear what 'opposite behaviour' means, a

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number of interpretations are possible. . . please clarify

5. Comparison of even-water. . . P 11 L 407: consider using 'precipitation' instead of 'moisture' P12 L 435, 442: I agree this is likely - as has been shown by Tweed et al. 2016 (Hydrol. Process. 30, 648–660 2016). It would also be relevant to cite this publication in the Introduction as it appears to be the first study using continuous real-time isotope monitoring to trace contributions to storm flow. P 13 L 463 and Figure 9: Event #7 results ( $\gg 100\%$  event water) needs commenting on. . . P 13 L 466 onwards: Seems unlikely there was spatial variation in rainfall in such a small catchment ( $\approx 0.5$  km<sup>2</sup>). Possibly O and H isotope compositions of other contributing (but not measured) water sources (groundwater, soil water, over land flow) had variable d18O / d2H relations (d-excess values). Since these were not accounted for the simple two-component fraction calculations based on O and H could differ. P 14 L 523: Somewhat ironically this section concludes that 3-hourly sampling would have been sufficient to capture the stream water events and would result in similar calculated event-water fractions. Consequently the stream data could have been monitored using a conventional auto sampler at relatively low cost and with much simpler operation. While this may not be the case in all storm water events it may be the case that it is precipitation monitoring that will benefit the most by continuous isotope instrumentation due to the very rapid (minutes) changes that can occur in precipitation isotope values.

Concluding remarks: The limitations regarding field deployability of the system (my general comments) and possible options for improvements in this regard could be expanded upon.

Table 2: stream stage unit must be m (not cm) Figure 3: Note that the recorded water vapour concentrations ( $\approx 18,200$  ppm) corresponds to a T of  $\approx 16.2$  oC supporting the explanation given by the authors that water warmed up beyond the 15oC setting of the diffusion cell of the CWS Figure 6: GMWL and LMWL require references (especially the latter) Figure 9: Error bars and their large variation between events need mention in legend and main text Figure 10, 11: Legends should clarify that the 3, 6, 12, 24 hour

'sampling intervals' were derived by re-sampling of the 30 min data

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