Author Response to hess-2013-422 - Referee 1 Comment

We appreciate the thoughtful comments of the Anonymous Referee #1 that address important issues particularly regarding the long term applicability of the presented monitoring system that may have been insufficiently addressed in the present version of the manuscript. Please find below our replies to the comments.

Comment #1:

The authors state repeatedly that the system can be used unattended for a long period of time and yet report data from only a single day. Where is the data to support the claims of long-term, unattended field use?

Reply:

Please note that the monitoring system uses an automatic valve switching unit based on a microcontroller and solenoid valves enduring $>10^9$ switching cycles. Thus, in principle, the system may operate without user interaction for any time period, limited primarily by the need to refresh dry gas supply and calibration standards (see reply to Comment #3) and less by the life span of the individual instruments (with the vacuum pump being the likely limiting factor, having an estimated life span of 10^4 h) or the probes themselves (due to the choice of materials, comparable durability to conventional soil physical probes can be expected, i.e. several years). The only other limiting factor is power supply for the isotope analyzer. We chose to show data from a single day of field measurements during which intensive destructive sampling was conducted, facilitating evaluation of the in-situ sampling results against a reference method. Since we applied the system in a remote field situation without access to grid power, gap-free continual monitoring was not possible but application was limited to sampling campaigns of several days or weeks. However, besides the issues raised by the reviewer in Comments #2 and #3, the authors believe that no indication exists as to why the system may not be applicable for long time periods occasionally intermitted by above named maintenance requirements. We are also currently preparing a paper where we used several weeks of measurements with the system in the field to monitor isotope tracer experiments. Since this dataset is supposed to be shown in relation to the scientific question of the new paper, we would like to avoid showing this dataset in this paper.

Nevertheless, the authors agree with the reviewer in that this aspect is important and the above named limitations will be discussed in the paper.

Comment #2:

The question of whether collection of pore water changes the isotopic ratios of the soil water has not been adequately addressed. I appreciate the analysis, but as this is perhaps the most serious concern with this type of measurement, experimental data is warranted.

Reply:

We appreciate this comment and agree with the reviewer in that this is an important issue particularly regarding the longer term applicability of the sampling method and the provided estimate of repeated measurements feasible at a specific location without causing significant isotopic enrichment of the local soil water can clearly only be seen as a rough indication. However, it should be noted that repeated measurements at identical locations presented in the paper did not show any enrichment effects for the later samples. We have also conducted several measurement with a sampling duration of >30 min as well as approx. 20 repeated measurements over a period of a few days at individual locations in both natural soil and the calibration boxes without observing any obvious enrichment effects of the soil water in the vapor isotope signal. Similarly, Rothfuss et al. (Water Resour. Res., 49, 3747-3755, 10.1002/wrcr.20311, 2013) recently reported that even in relatively dry soil no continuous enrichment was observable after four hours of continuous sampling using a similar method.

It is understood that these results do not fully clarify the warranted issue raised by the reviewer in that the presently available data does not allow for an estimation of the maximal number of repeated samples without inducing soil water isotopic enrichment. Yet, they show that no significant enrichment of soil water may be expected for typical individual sampling periods and give an indication of the minimum number of feasible undisturbed samples (i.e. this may be estimated as the ratio of continuous sampling time without enrichment and the individual sampling time). If we consider that non-detectable small local enrichment effects will be evened by induced transport processes in the soil water and vapor phase over time, the total measurement time during continual rather than continuous sampling may be estimated to be even significantly longer. Further following this line of reasoning, once the sampling time at a given location per unit time is sufficiently low and individual sampling times are sufficiently short, we would not expect enrichment of the local soil water at that location. Thus, the question becomes more one of the feasible sampling frequency rather than the feasible number of individual samples without causing enrichment.

As we agree with the reviewer concerning the importance of this issue, this should be discussed more clearly in the manuscript and the potential limitation on the sampling frequency should be indicated. We also agree in that this aspect should be further assessed experimentally in the future. Since the maximal sampling frequency will depend upon both operational (e.g. extraction rate) and natural (e.g. soil water content, temperature) factors determining the available water reservoir and the extracted amount of vapor, this issue clearly deserves further yet specific investigation.

Comment #3:

Similarly, the lifetime of the calibration setup has not been determined or discussed. After how many measurements have the isotope ratios of the calibration boxes changed to a

degree that new boxes must be prepared? How significant, in time and cost, is this box preparation?

Reply:

The reviewer makes a warranted comment here and we agree with the reviewer in that the limited period of usability of a prepared set of calibration boxes should at least be discussed (see also replies to Comments #1 and #2). In contrast to the case discussed in reply to Comment #2, an actual limit not only on the frequency but also on the number of samples that can be extracted from these boxes exists due to the limited water reservoir present in the boxes and this should be clarified. To provide a rough impression, we can use the estimated volume of liquid water extracted per sample (i.e. 0.4 mL assuming 20°C and 1013 hPa) to compute that the bulk water reservoir within a calibration box would have been reduced by <2% after 10^5 calibrations.

The effort in time and cost to prepare the boxes is low. The initial set up of the boxes themselves requires approximately one or two hours of work and no more than 100 $ of monetary effort (excluding the soil physical and soil water isotope probes). The time required for collection of soil material for filling of the boxes will clearly depend on the field situation and cannot be generalized. The preparation of the boxes for a specific application requires approx. three hours of work for drying the soil material, filling of the boxes, and addition of calibration standard waters. The material maintenance cost is limited to purchase of reference waters or non-existent if cost-free sources (e.g. snowmelt, sea water) can be used.

Comment #4:

It would be helpful to see a comparison between the exponential fits used in the manuscript to determine the asymptote and the use of an average value recorded after the sample value has leveled off. The authors have not quantified the improvements gained by using the exponential fits, nor proven the robustness of the fitted numbers (ie, how sensitive is the final value to changes in the sampling period)

Reply:

The authors agree with the reviewer in that a systematic assessment of the exponential fitting results versus simple arithmetic averages as well as of optimal sampling duration and time span used for fitting would be beneficial. Please note, however, that the provided summary statistics of measurement accuracy and precision give a good indication of the data quality that may be expected by following the procedure described in the manuscript. Also, as outlined in the discussion, it was for us of great importance to use short sampling periods regarding the imposed disturbance on the natural water-vapor system (see Comments #2 and #3), changes in the targeted soil water vapor isotopic composition or other effects that cause signal variability, and of course to attain a high sample generation rate. Please be

aware that we do not claim that this is the optimal data processing method that can be used or that the chosen trade-off between sampling time and data quality is optimal, which in addition will certainly depend upon a variety of factors. Given these aspects and the current extent of the paper, we believe that such an analysis – while certainly worthwhile on its own – may not be necessarily required to warrant the functionality of the presented method and may exceed the scope of the work presented. However, we are in fact presently preparing a set up for a systematic assessment of optimal sampling and analysis procedures that will also yield a more suitable data source for truly practicable conclusions. In the same context, we intend to assess the maximal sampling frequency and time span of calibration box usability (see replies to Comments #2 and #3). The authors are fully aware of the fact that the functionality and limitations of the presented monitoring system have not been assessed holistically and neither has every aspect been optimized and the system will certainly profit from further experimentation and application.