Author responses to reviewers
(Reviewer comments in italics)

Both reviewers recognize the uniqueness of the data and the importance of the analysis of both variations in the vertical structure and the advanced approach to undertaking the surface flux partitioning problem. Both reviewers provide a number of points that help strengthen the analysis, and by and large, all suggestions have been included. Both reviewers also point to a number of specific areas where additional detail on the limitations with data and discussion of consequential confidence in conclusions may arise. This has been added. By and large, all reviewer comments and suggestions have been adopted.

Anonymous Referee #1
Received and published: 24 July 2012

This manuscript makes use of relatively high-frequency measurements of deuterium in water vapor from a very tall tower research facility in Colorado. Combined with other pieces of information (isotope ratios of a decaying snowpack, meltwater ponds, etc.) the authors attempt to determine/constrain the sources of water vapor in the atmospheric boundary layer. The underlying scientific rationale for the investigation is related to the argument that: : : "inadequate representation of surface fluxes and their dependence on surface conditions are among the key sources of uncertainties in quantifying regional hydroclimate". Here, isotope measurements throughout the atmospheric boundary layer in combination with "mixing line" analyses are used to help constrain the various surface contributions (evaporation, sublimation, etc): : :.i.e. reduce uncertainties in the representation of the surface fluxes. Overall, I like the subject of the manuscript and provide the following comments/criticisms:

1.The introduction, methods, and discussion sections omit numerous key references related to the discussion of mixing line (Keeling plot, gradient, flux ratio) analyses. Since 2004, work by Griffis, Lee and others have involved laser-based isotope flux measurements of 18O-CO2, 13C-CO2, 18O-H2O etc. The rationale for flux- based approaches has been discussed in detail and the limitations of Keeling/mixing line analyses have been well documented- especially for water vapor where the two end-member mixing assumption is certainly violated. The similarity assumptions in terms of turbulent transport for each isotopologue have also been discussed. Griffis applied the flux gradient approach on a tall tower and compared it to eddy covariance based isotope flux ratios of 13C-CO2. The work by Lee et al., 2006 (Tellus); 2012 (Boundary-Layer Meteorology, in press) has demonstrated that the Keeling approach (when time-based,1 measurement height as a function of 1/concentration) is not reliable for water vapor or at best can only be applied for a narrow range of environmental conditions.

The additional citations have been added.

2.Performance of the Picarro L115-i. To what extent is this analyzer stable/reliable under field conditions? How does changing ambient temperature impact the measurement? To what extent do vibrations associated with its movement impact the measurement? To my knowledge, changing temperature and vibrations could have a detrimental impact on the optical alignment, fringing etc. These issues should be addressed. Further, how does the calibration method account for the changing mixing ratios observed over the 300 m profile?

The method and appendix describes the performances characteristics and calibration, and one can therefore be confident in the instrumental results. We now better articulate the potential for issues (i.e., higher uncertainty) with respect to drift. The text now cites a few papers from the growing literature base that shows similar performance statistics to those we find. We are of course aware there is strong potential for sensitivity to temperature variations during diurnal cycles, and potentially vibration in the instrument. Rather than being resolved, drift effects becomes part of the total uncertainty estimate. We find that drift and other unresolved uncertainty are particularly important for deuterium excess, rather than a single isotope ratio. Due to this we focus here only on a single isotope ratio, δD. This is now explained in the text.

The appendix provides an explicit description of how account was made for the changing mixing ratios. "Raw δ (both D and ^{18}O) measurements are corrected to remove measurement dependence on mixing ratio…"

3.Have other investigators used this Picarro analyzer for insitu field measurements? What were the performance characteristics, reliability?

The analyzer model has been used elsewhere (for instance, Gupta et al., 2010; Noone et al., 2011), and the specific unit in question (i.e same serial number) remains in field use (papers in prep.). More broadly, this is a well-known commercial instrument that is beginning to be widely deployed. The appropriate core citation is Gupta et al., (2010). The present paper describes the calibration approach as implemented for this study to achieve the required performance in this application (see also comments below), and quotes the relevant performance statistics. There is a growing body of published work by other groups also using this type of instrument.

4.Profiles. My understanding is that it takes 15 minutes to obtain a profile. The elevator takes the instrument on a 9 min ride to the top where it sits for a 3min measurement interval and sits at the bottom of the profile for 3 min. Based on the turbulent time scale – can you obtain a reliable gradient with this type of sampling scheme?

Yes, although the purpose of the paper is to help enlighten some of the issues with regard to temporal variation versus steady state in doing so. (Just as Griffis et al., has shown for ^{13}C). It is appropriate to keep in mind the time scales of approximately 30 minutes are typical of those resolved by, say, eddy covariance methods. Our approach, and any profile approach considered to date, is similar if a single gas analyzer is used. Again however, a central point of the paper is in demonstrating the limitation of gradient methods associated with non-stationary flow. Because this intent was unclear to reviewer, we've endeavored to make this clearer as an explicit aim of the paper, rather than delaying until the concluding discussion to make the point.

5.Equations 4, 5, 6. If using the flux ratio method, the transport coefficients can be neglected if they are the same for each isotope (i.e. assume similarity). In your equations this scaling applies in the surface layer, but is it valid in the mixed layer?

Yes. Noone et al., 2011 shows that the general mixing approach is valid on all scales. The surface layer being a clear example. The text now makes this clearer (end of section 2.2). The relevant question is if the 2-member mixing process is appropriate. A result demonstrated in this paper is that is not.

6.Mixing line assumptions. It is difficult to accept that a two end-member mixing model could be applied anywhere with reliability. i.e. there is entrainment, advection, and multiple surface sources so how can such a model be justified?

Agreed. It is better to think of this as the null hypothesis. There are certainly cases where it can be applied, and these instances are themselves interesting. The observations we present, however, demonstrate where it fails, which is more typical and is a goal of the paper. It is noteworthy that there is presently no alternate theories to simply describe isotope (or any trace gas) variability within the boundary layer beyond that which one could clean from explicit forward modeling. One objective of the paper is to point out this shortcoming, and begin to map a pathway forward.

The final paragraph of the Method section 2.2 states “Given that the simple mixing configurations discussed assume stationary end members, assessing the fidelity of mixing line methods comprises identifying changes in the mixing line end members.”

7.There is a need to comment on the footprint of the tall tower observations. These will differ dramatically for concentration vs fluxes. There is also a need to provide some information regarding the source footprint that influences these tall tower measurements. What are the surface conditions that influence these measurements? Snow packs are highly variable and their decay typically forms a complex patchwork on the landscape. One can imagine that the isotope ratio of the snow pack, ponds, bare soil etc are highly variable in space and time. There should be supporting information in the form of land use/land surface conditions derived by satellite.

Now given. This is known from previous trace gas studies at the site and is 10s of km.

8.Throughout, it is not always clear if the mixing line refers to gradient or traditional Keeling type analyses. Further, it is not always clear if these two methods are being applied within the surface layer or mixed layer. These terms and their use should be made clear throughout. It is only later in the manuscript that specific heights etc. are noted with more detail.

A revised manuscript has ensured we always say “gradient” versus “temporal”. In short, we seek to always use the gradient method, except where it is contrasted to the temporal approach which broadly is unreliable.

9.What are the typical heights of the convective and nocturnal boundary layers and how does entrainment/top-down diffusion impact the results (i.e. what is the isotope ratio of the vapor in the layer of air being entrained through daytime mixing).

Unfortunately, the SODAR operating at the site was not functioning reliably during this time period, so we cannot observed the PBL height when it is higher than the tower. However, we now have a sentence that quotes the mixed layer height and show the PBL depth based on Richardson number as a guide for the nocturnal and growing case. The question of entrainment is discussed in the context of the example profile data. Indeed, on aspect of the presented work is the use of the CO2 tracer information to help distinguish the dynamical layers.

10.Mass balance assumptions – surface runoff seems like a key component since the soils are still frozen and there is limited infiltration. What is the spatial extent of the snowpack isotope ratio observations? I see no mention of how these were sampled spatially or temporally. I know from person experience that vertical variations in isotope ratios are very strong – this raises the question of what is the surface and where does sublimation originate from.

This is an important point to consider. A full examination of the snow morphology is not appropriate here. However, we have endeavored to improve description of the method and where limitations in the sampling method may impact the results. The vertical heterogeneity is likely important. Indeed we have seen significant vertical variation in snow isotope ratios in work since this 2010 experiment in other settings (Colorado alpine environments and Greenland in particular). In the case examined in the paper, however, the snow pack is rather shallow. Starting from about 10 cm, becoming patchy, then dwindling to nothing. Practical sampling issues also limit the dataset. Specifically the temporal snow sampling we performed during the experiment was done by opportunity and focused on capturing characteristic values of the snow pack rather than adopting a sampling method to target resolving time variation in the snow pack profile. This is now better described in the methods. The question of the depth profile is particularly intriguing, though, and a topic of continuing work.

11.Why is there no mention of the actual total flux observation from the tall tower? How large is the total latent heat flux that is to be partitioned? Given the amount of energy available for this time of year it seems like it will be very small (a few W m-2) and that partitioning this small uncertain flux is limited by its own uncertainties (large error in isotope composition of flux, varying end members on short time scales etc.).

At the time of the experiment, there was no latent heat flux or sensible heat flux measurement available (via eddy covariance, or other closure methods). While the issue of energy partitioning is certainly relevant, so too is assessing the distribution of water on the landscape. The present study focusses on that component. New work based on additional measurments now being made seek to advance understanding of the energy partitioning, and is the topic of forthcoming manuscripts.

12.Kinetic effects. How does turbulence influence the fractionation associated with sublimation and ponding water evaporation. I did not see that this was discussed, but would need to be parameterized for the landscape by taking into account factors such as snow roughness length etc.

Perhaps, but this is largely unknown. The model here uses established theory to account for the kinetic fractionation (equation 14, for instance). The model developed does not appear to require strong kinetic fractionation to explain a single isotopic species. This need not be the case if one were to consider the deuterium excess, of course. The broader question of fractionation during sublimation is discussed, and is a more relevant concern here. The revision has now pointed out that the treatment of kinetic effects is likely incomplete.

13.Page 16344 section 20. Good point, but this section should be cited appropriately.

The text now point to the results from other work using continuous sampling, which have similar findings, with citation to Griffis, Lee et al., work.

14.Conclusions. Page 16349 Section 5-10 This not a novel finding. Section 15 – this is weak as written because it does not discuss source footprint differences etc. Section 20-25. – this section ignores previous research.

The section is question is a summary statement from the field measurements. The text has been now indicates that this is the case. The link between the boundary layer dynamical structure, intermittency and trace gas distribution is not widely acknowledged. Naturally, once one thinks of this linkage it appears obvious. Certainly the features should appear in any dataset measured from tower of appropriate height (i.e., above the surface layer). However, these observational features are linked to known dynamical characteristics of the boundary layer. Previous work on transport based on long integration times certainly recognize this potential impact of boundary layer dynamics (entrainment, advection, intermittency, etc.), and there is a wide group of papers that make this point, or indeed try to quantify it, for the case of CO_2 in particular. Some are now cited. The examination of the evolution of the mixing lines is a particularly novel aspect of this paper, and has not been done before. It certainly has been suspected, and again, once sees this evolution it confirms what has been proposed from previous work without the advantage of time/height data like we present. Some previous work has used more than one inlet height to look at gradient mixing lines, however, those studies cannot remove the evolution of the profile due to lack of vertical resolution. Limitations in previous work is now cited.

The footprint is now given in the methods section, and a reminder is given here in the conclusions.

15.I wonder if the 18O-H2O data would provide similar information and partitioning or would we arrive at a very different conclusion?

An analysis based on ^{18}O would produce similar results, within the uncertainty, because of the limited role of deuterium excess in the analysis. One reason for using D rather than ^{18}O is that the kinetic effect is smaller, and therefore the results more robust in light of possible uncertainty that arises from kinetic fractionation. As a sanity check, inspection of the deuterium excess shows conceptual consistency with the findings provided, and indeed we have used the excess to provide a qualitative check on the results where possible. However, we are uncomfortable with the quantitative aspects of deuterium excess data. There do appear to be some unresolved artifacts associated with instrument drift and precision that limits the usefulness of the deuterium excess, as noted. For this reason we focus on a single isotope. However, strong qualitative agreement with the analysis performed here provides confidence. For instance synoptic variability in the deuterium excess is very distinct and matches expectations for shift in marine sources (including values near 10 permil with oceanic origin, and higher values resulting from evaporation). However, vertical gradients are very weak, and typically of the same size of the uncertainty in the excess (a few permil). Therefore, we are uncomfortable attempting to extra additional quantitative constraints from the deuterium excess at this time. For this reason, it has been excluded from the paper.

Anonymous Referee #2

Received and published: 3 September 2012

The authors present an interesting set of data, including stable water isotope measurements, from a tall tower near Boulder. To my knowledge such data are unique, and the measurements used to address a relevant problem. The writing is mostly clear, also there remains room for improvement, as explained in the main points. There are also several other minor points that should be addressed by the authors in order to improve the quality of the manuscript, as detailed below.

Main comments

1. Vertical resolution

The biggest limitation of the data set is the fairly low vertical resolution of 27m. In particular sharp gradients in stable conditions and in the surface layer are thus probably completely smoothed out. Could the Licor humidity measurements allow for (qualitatively) recreating some of the sharp gradient structure? This limitation of the data set is worth more discussion. How limited is the flux-gradient relation when the profiles have been smoothed so strongly?

In the presentation of the results, it is not always clear where you consider the boundary layer height to be situated, and how it relates to the surface layer. From your dataset, it would be easy to estimate the boundary layer height (e.g. from calculating a Richardson number) and to plot it e.g. in Fig. 3. Also, Fig. 3 could be clarified by using more distinct color shadings, and by not showing the bounding contours of the shading (these are easily confused with the potential temperature contours).

The resolution limitations are now noted in section 3.3. The native resolution of the data is approximately 5 meters. The smoothing that results from the calibration effectively reduces this, but the true resolution of the resulting data depends on the optimization of the structure function used memory correction. Importantly, the method by design preserves gradients much better than anticipated from simply having measurements at 11 different heights. The quoted value of “effective resolution of 27m” is a statement of degrees of freedom, not the true vertical spacing. Nonetheless, the comment that better resolving the profile structures would be preferable is certainly valid.

It is easy to show, and conceptually visualize, the smoothing data using simple algorithms has the same influence as a diffusive processes. Therefore, mixing lines would be preserved to the level of smoothing. Similarly, typical gradient methods use a regression fit to obtain the perturbation quantities (u^*, q^*, δD^*, etc). This is, in effect, a smoothing (i.e., an average slope is found from multiple observations). The approach here has this in mind in the use of the memory correction function. Therefore while the final corrected values have 11 degrees of freedom, the quality of the “slope” information is high.

> Could the Licor humidity measurements allow for (qualitatively) recreating some of the sharp gradient structure?

Yes. The paper now points out the agreement between the Licor and Picarro data. We don’t include any further analysis of the high frequency Licor data, as it is not required for the present study. Specifically, we’d prefer to focus on the isotope relationships where we have data available. There is a rather interesting extensions to the present work looking into the role of small (cm scale) turbulence near stable layers on gas transport (H_2O and CO_2, for instance). High speed data from an open path sensor would be one way to look at this.

PBL height is now plotted, and based on the Richardson number. We checked that the computed values are in reasonable agreement with sonic backscatter from a nearby sodar. Sadly the sodar was not operating properly during this time period, so it not particularly useful for a direct estimate of PBL and mixed layer height.

2. *Calibration procedure and isotope measurements*
As I understand from Appendix A the instrument was not calibrated during the field campaign, which does not allow to correct the data for instrument drift. This seems however recommended, as Aemisegger et al have shown recently for the L1115-i. It is probably a good idea to explain how your calibration strategy differs compared to their study, also since you mention the quality of calibration procedures as an important prerequisite for deuterium excess measurements in the Conclusions. In the beginning of the manuscript 18O and the additional information from deuterium excess are quickly dropped from the discussion without it being made clear why that is the case. Rather than leaving the reader guessing that the calibration procedure might be the reason, it should be spelled out clearly. Are the humidity data shown in Fig. 3 from the L1115-i or from the Licor instrument? How well do the two humidity measurements agree?
There are no data gaps in the profile time series: was there no situation where windshading from the mast occurred, or were these situations not filtered out?

In the methods we now state that the LICOR and Picarro H2O is in agreement. We found this same result using a Licor 7000 (Noone et al., 2011). Both instruments, however, need to be calibrated to the same (linear) scale. It is it is not surprising that they can be made to agree.

There is somewhat of a cottage industry in describing how to calibrate this type of isotopic instrument – a number of papers have appeared in print over the last year, and some of which are cited. The particular paper mentioned by the reviewer was not published when the present paper was submitted, but is another example. It is now included in the reference list. Rather than point out all the differences with all the methods, we cite a handful of other papers that have similar corrections and note the similarities. The method described includes a comprehensive treatment of uncertainty by using a Monte Carlo method. Other methods are likely overly optimistic in constraining the uncertainties using linear error propagation assumptions. If this is done correctly, linear methods would overestimate the uncertainty. We have two further papers in preparation which describe calibration procedures in detail, with different trade-offs to avoid computational limitations associated with Monte Carlo methods. Rather than making light of the analysis in this paper, we prefer to retain only sufficient detail in the appendix, and reserve a full description and methodological study of calibration methods for another paper. The revised appendix should satisfy the reader since it builds on previous methods, and yet is sufficiently brief not to detract from the object of the present manuscript to perform the analysis.

3. Details on the meteorology
The discussion of the meteorological situation in Sec. 3.1 is very qualitative. This could be considerably improved by providing details e.g. on how cold the "strong surface cooling" was, how cold the "cold nighttime temperatures" were, etc. It is difficult to pick this out from Figs. 3 and 4 alone. The writing from Pg. 16340 L. 20 onwards needs improvement.

Some additional quantitative statements have been added, particularly in regard to temperature changes at the surface. While this can be read off the figure, having the number at hand as the reviewer

suggests is useful to illustrate the magnitude of the cooling. The meteorological description is intended to provide context to the isotopic analysis, and so by design is mostly descriptive.
A redrafting of the paper has included many minor changes to refine various phrases, including some in this section.

4. Clarification of the Rayleigh model
In Sec. 3.1 / Fig. 5, a Rayleigh model is used to match the observations. Can you clarify here what is meant by "precipitation efficiency", and what the implications of that model parameter are for the data? Also, is the match of moisture source temperature and relative humidity unique or could other combinations also yield plausible distillation curves? Also it should be mentioned that mixing during such a long transport distance of water vapor to the measurement site could have altered the isotopic composition. It is not clear how the last paragraph in Sec. 3.1 relates to the previous discussion.

Precipitation efficiency is defined as the focus of a paper elsewhere, to which the reader is referred for details (Noone 2012). We now say “partial removal” to help orient the reader. Similarly, the physical intuition that advection of water as clouds liquid condensate is now stated. The final paragraph has been rewritten to point explicitly to Figure 5 for the points associated with the front on 18 February. The conceptual importance for the agreement with a Rayleigh process is expressed: i.e., a continually precipitating air mass that moved from the oceanic source to the south.

5. Detailed comments

Pg. 16341, L. 26: and ARE indicative Pg. 16341, L. 29: and IS shown Pg. 16342,

Fixed.

L. 13-14: I can’t see an upward propagation here, as the whole profile shifts to less depleted values than the time before

The text now notes the shift in the mean value of the profile, as expected in the case of strong mixing.

Pg. 16344, L. 26: The writing from here to the end of the paragraph needs clarification/improvement

Edited for clarity during revision.

Fig. 9: use solid lines instead of stippling, can’t see a brown square. Shading does not show in print.
Corrected. Shading will be checked on proof copy.

References
Aemisegger, F., Sturm, P., Graf, P., Sodemann, H., Pfahl, S., Knohl, A., and Wernli, H.: Measuring variations of _18O and _2H in atmospheric water vapour using two commercial laser-based spectrometers: an instrument characterisation study, Atmos. Meas. Tech., 5, 1491-1511, doi:10.5194/amt-5-1491-2012, 2012. Meas. Tech., 5, 1491-1511, doi:10.5194/amt-5-1491-2012, 2012.

Added, as requested.