

1 **Anonymous Referee #1**

2 Received and published: 28 July 2016

3 **General comments:**

4 The study "Response of water vapour D-excess to land-atmosphere interactions in a semi-arid  
5 environment" by Parkes et al. analyses the interplay between changes in atmospheric moisture  
6 isotopic compositions and the impact of local scale forcing of evapotranspirative vapor isotopes. As  
7 recently the isotopic composition of atmospheric moisture has been proposed as a tracer of large scale  
8 moisture recycling, this is an interesting topic. Also, apparently the impact of isotopic compositions  
9 was often studied using modelling approaches, which is rather surprising to me, given the increasing  
10 amount of isotopic ET studies recently! The overall quality of the paper notwithstanding, I see quite  
11 some space for improvement both technical and content related.

12 *We appreciate the reviewer's comments and thank them for their time. Our comments and*  
13 *responses are shown in italics.*

14 *With respect to the reviewer 1's general comment "Also, apparently the impact of isotopic*  
15 *compositions was often studied using modelling approaches, which is rather surprising to me,*  
16 *given the increasing amount of isotopic ET studies recently!", we are unsure of the reviewers*  
17 *meaning or the section of the paper they are referring to. Perhaps they refer to the sentence in the*  
18 *introduction ( lines 113-115) that states "The studies of the diurnal cycles have largely relied*  
19 *on isotopic models to assess the contribution of ET fluxes, but a lack of dET measurements make*  
20 *it difficult to draw robust conclusions." This is true, as the papers we refer to (which study the*  
21 *diurnal cycle of  $d_v$  and the role of ET) have used process based models (Welp et al., 2012),*  
22 *empirical models (Simonin et al., 2014), or provided an interpretation of their data (Zhao et al.,*  
23 *2014) without providing any direct measure of D-excess in ET.*

24

25 1) In my opinion the study campaign was rather short, only 2 weeks roughly, and to my mind the  
26 significance of the interpretation is hence limited.

27 *While the study period was relatively short, our study was completed in a remote semi-arid*  
28 *environment. These ecosystems are largely under-represented in isotope literature, especially*  
29 *within Australia, and also in using in-situ analysers. Given the duration, we do not make any*  
30 *major conclusions or claims about impacts on the hydrological cycles. Indeed, we deliberately*  
31 *focused the conclusions so that they relate to the specific meteorological conditions observed*  
32 *during the experiment (quiescent meteorology and extended dry periods, which are common to*  
33 *semi-arid environments) and what these might mean more generally for  $d_v$  and  $d_{ET}$  variability*  
34 *over the longer term, as well as for other conditions and environments. We believe that this is an*  
35 *important and quite novel set of results.*

36 *Beyond the ecological setting of our study, providing direct measurement of  $d_{ET}$  is also novel, and*  
37 *shows that for our location and meteorological conditions, ET does not cause the relatively high*  
38 *D-excess values. We believe this is a useful and interesting finding, especially when in terms of*  
39 *providing context to other studies of longer duration and in different locations (e.g. Bastrikov et*  
40 *al., 2014; Simonin et al., 2014; Welp et al., 2012), we observed a very similar diurnal cycle. We*  
41 *have used section 4.2 in the discussion to elaborate on the context of our work: in particular, the*  
42 *long dry period leading to very low soil moisture D-excess values and how this may be applicable*  
43 *elsewhere. We will modify section 4.2 to include comments on the duration of the observation*  
44 *period and further emphasise the context of our measurements.*

45 2) I have some methodical concerns regarding laser spec calibration and chamber construction  
46 (see detailed comments).

47  
48 *Fully addressed below for relevant specific comments.*

49  
50 3) To my mind both results and discussion section are rather long and very detailed. Moreover,  
51 quite often results are repeated within the interpretation section, making the manuscript rather  
52 hard to follow at that point (very unlike the intro and M&M part btw.). I suggest to focus on  
53 the main results and shorten both parts to make it easier to follow.

54  
55 *Comments noted and we will streamline results and discussion sections where appropriate.*  
56 *We will ensure that results are not over-repeated within the discussion section.*  
57

### 58 **Specific comments:**

59 48ff: Be more specific! How?

60 *Sentence modified – “Spatial and temporal variability of D-excess in ET fluxes therefore needs to be*  
61 *considered when using  $d_v$  to study moisture recycling and during extended dry periods may act as a*  
62 *tracer of the relative humidity of the oceanic moisture source.”*

63 60ff: I think this is a bit overstated, there are surely some examples here!

64 *We have clarified this sentence to reflect that datasets directly quantifying land-atmosphere exchange*  
65 *processes are rare – “To do this effectively, a range of datasets that directly quantify a variety of*  
66 *processes represented within these models are required. Unfortunately, datasets that directly measure*  
67 *land-atmosphere exchange at the process level are limited.”*

68 63ff: Shouldnt this be 2 sentences?

69 *We are not sure what the reviewer is referring to here, as this is already two sentences.*

70 73ff: how about transport processes? i.e. kinetic fractionation?

71 *We have changed the sentence to include ‘equilibrium and kinetic isotopic fractionation’ i.e. “The*  
72 *utility of water isotope ratios for tracing sources of moisture derives from the characteristic*  
73 *equilibrium and kinetic isotopic fractionation that occurs when water undergoes a phase change,*  
74 *causing light water molecules to preferentially accumulate in the vapour phase.”*

75 81ff: Again, doubt there are so few. How about Berkelheimer, Simonin, Welp and others?

76 *Our statement is that there are relatively few studies using vapour, relative to precipitation focused*  
77 *studies. The references mentioned by the reviewer do indeed discuss land atmosphere exchange for*  
78 *vapour isotopes, and we have referred to these in other sections of the manuscript. We have added*  
79 *(e.g. Aemisegger et al. 2014; Risi et al. 2013) to indicate some of these related studies.*

80 98: Suggest to change "given this" to therefore

81 *Noted and adjusted.*

82 140: have has? omit has?

83 *Noted and adjusted.*

84 168: If you indeed did not calibrate or drift check the LGR i think your values have a high  
85 uncertainty. I.e. the average difference to the Picarro might be small but you standard deviation

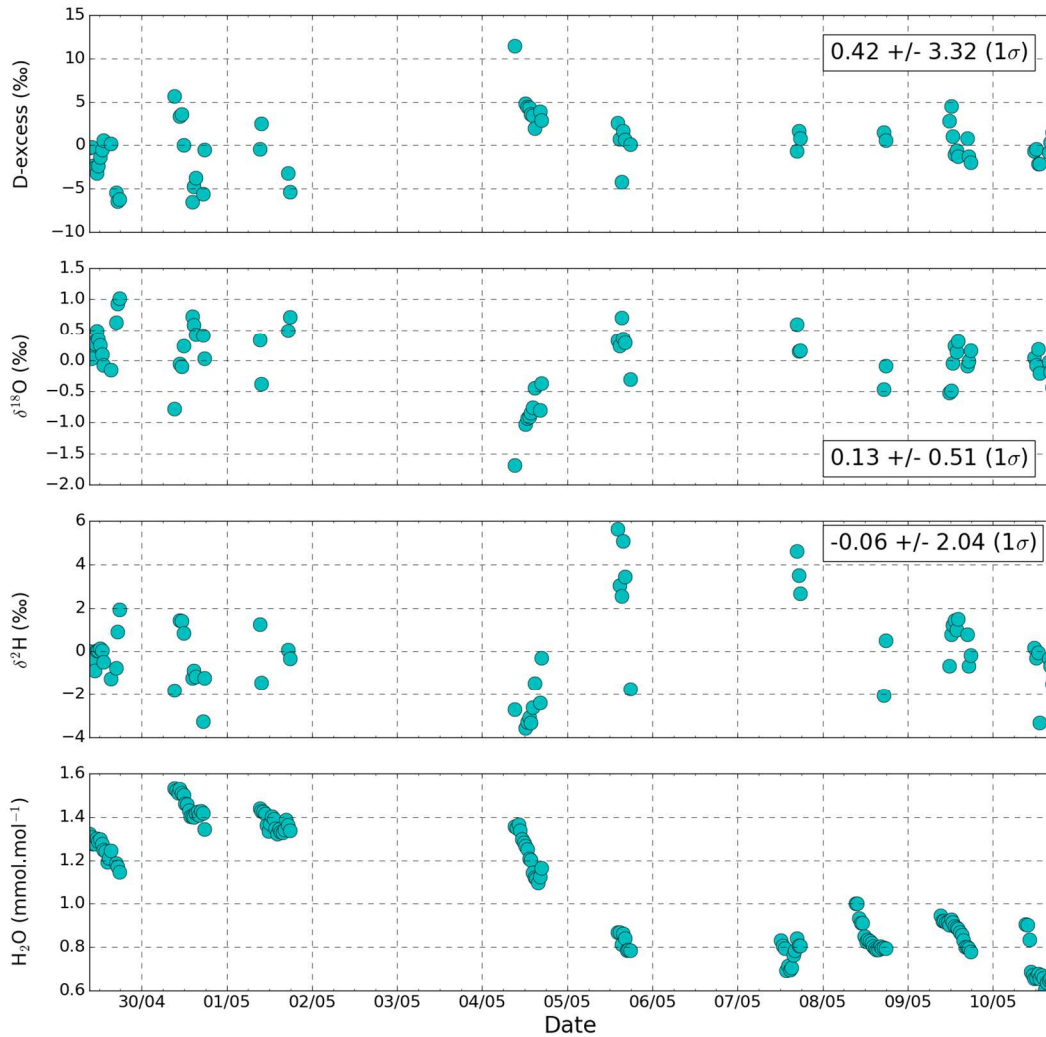
86 suggests there was a high point to point difference. At the least it would be nice here to see the time  
87 evolution of the difference between laser specs throughout the campaign!

88 *We are not sure if the reviewer is questioning whether we present raw LGR data (i.e. no calibration*  
89 *corrections applied) or whether there were no calibrations run during the campaign period. As stated*  
90 *in the text (section 2.2.1), we calibrated the LGR in the lab before and after the campaign to develop*  
91 *corrections for water vapour cross-sensitivity and linearity. This was completed simultaneously with*  
92 *the Picarro. During the campaign no calibration experiments were completed for the LGR, but to*  
93 *determine the importance of instrumental drift for our measurements, we regularly ran the two*  
94 *analysers simultaneously sampling ambient vapour (lines 180-188).*

95 *Reviewer 1 raises an important point regarding the drift for the LGR. While on average the Picarro*  
96 *and LGR agreed over the campaign, there was some shorter term drift that led to differences between*  
97 *analysers: most likely the result of the LGR's large temperature dependence. We did not include a*  
98 *comparison of the two analysers, as the differences between them is defined mostly by scatter with no*  
99 *clear trends. Interestingly though, there is no relationship between differences between the analysers*  
100 *and the major shift in H<sub>2</sub>O concentration (i.e. wet vs dry period). This indicates that we have*  
101 *accurately characterised the water vapour cross-sensitivity of the two analysers and that this*  
102 *correction was stable throughout the campaign.*

103 *In line with Reviewer 1's comments we will include a figure showing the time series of differences*  
104 *between the two analysers over the campaign (see figure 1 below). So as not to detract from the main*  
105 *message of the paper we will place the figure and discussion of its consequences for our*  
106 *interpretations in the supplementary section. In constructing this figure we realised the biases listed*  
107 *in the paper were for the whole comparison period, which included nocturnal hours. This is not what*  
108 *we have indicated in the text (line 182) and is not a fair comparison for our measurements, as the*  
109 *LGR showed a very big temperature dependence that led to nonsensical values at night (hence our*  
110 *restriction of chamber measurements to 09:00 to 17:00). The comparison is more favourable during*  
111 *the day when the LGR cavity temperature was relatively stable and chambers measurements were*  
112 *made. We will update the bias statistics to the values shown in figure 1 below.*

113 *In some cases the differences between ambient  $d_v$  and  $d_{ET}$  were quite small, so  $I_{ET}$  calculated for the*  
114 *D-excess could be strongly influenced by LGR instrumental drift. However, this does not affect our*  
115 *interpretation, as for all chamber measurements that passed our QC requirements D-excess*  
116 *decreased during the measurement, illustrating that ET always had a negative forcing on  $d_v$ . To deal*  
117 *with the uncertainty caused by the relative instrumental drift of the two analysers, we will include*  
118 *statements in the text emphasising that while  $I_{ET}$  would be influenced by drift, our interpretation of*  
119 *negative forcing remains the same.*



120

121 **Figure 1: Time series of daytime differences between isotopic measurements of Picarro and**  
 122 **LGR for periods when the LGR and Picarro were simultaneously sampling from the**  
 123 **meteorological tower. The H<sub>2</sub>O concentrations measured by the Picarro for these periods are**  
 124 **shown.**

125 207: Strong doubts concerning you placement of collars only 2 days prior to measurements! this will  
 126 surely cut roots and there will be some affects in that direction.

127 *We agree with the reviewer that collars were installed a relatively short time before the study period.*  
 128 *However, the vegetation consisted of grasses with shallow roots (~5cm), so while near the edge of the*  
 129 *chamber, roots may have been cut, the vast majority of the vegetation cover was unaffected. As with*  
 130 *all chamber measurements, the apparatus can influence the environment and thus fluxes, but these*  
 131 *would not change our interpretations here. We can add a sentence to include the reviewer's comment*  
 132 *on this issue.*

133 211: Did you coat the chamber in some ay? It is well known that Plexi exchanges water and acts like a  
 134 sponge creating a smearing effect in background chamber and vice versa transitions. This could  
 135 actually affect you keeling plots quite much.

136 *No, we did not coat the chamber to reduce memory effects. We assume the reviewers comments are*  
 137 *related to memory effects influencing ET isotopic compositions calculated from the Keeling plots of*  
 138 *chamber measurements. As the reviewer correctly notes, memory effects could have a major effect on*

139 *the determined ET isotopic compositions. Indeed, we considered this and to combat memory effects*  
140 *we employed high flow rates, as the high turnover rates will reduce such memory effects. We also*  
141 *developed quality controls for Keeling plots, ensuring linearity and a significant H<sub>2</sub>O concentration*  
142 *change was observed.*

143 *While memory effects are unavoidable and can influence ET isotopic compositions, they do not*  
144 *change our interpretation. Memory effects are likely to attenuate the slope of Keeling plots, thus*  
145 *reducing the disparity between ambient vapour and ET isotope composition determined from the*  
146 *intercept of these plots. This is because chamber walls retain the isotopic composition of the ambient*  
147 *vapour being mixed with the ET flux. So, while memory effects would cause a high bias for the*  
148 *determined  $d_{ET}$  (i.e. Keeling plots for the D-excess always had a negative slope), our purpose was not*  
149 *to assess absolute  $d_{ET}$  values, but to determine whether ET could cause the  $d_e$  diurnal cycle: in*  
150 *particular the high daytime values. As such, this interpretation remains unchanged.*

151 *Regardless, it is an important point and we can include mention of memory effects in the methods and*  
152 *relating our methodology to how these were dealt with. In the results we will review the consequence*  
153 *of these for our interpretations.*

154 230ff: Why did you choose the Keeling method? Why not a mass balance approach?

155 *Studies comparing the two methods have shown they are comparable (Lu et al., 2016; Wang et al.,*  
156 *2013);, which is not surprising, as they are based on the same assumptions (i.e. that background*  
157 *concentrations and isotopic compositions of source and background water vapour does not change*  
158 *during a measurement). The main difference is that the Keeling plot requires extrapolation to*  
159 *determine the intercept of the  $\delta_{chamber}$  vs  $1/q_{chamber}$  plot. Comparisons in the literature have shown they*  
160 *agree well in practice. Considering the focus of our work was not to evaluate the two methods, we*  
161 *only present data using the Keeling model. In addition, as discussed in lines 237-256, we developed a*  
162 *filtering approach for the Keeling model focussing on ensuring linearity of our Keeling plots. We will*  
163 *add a comment to indicate that we considered mass balance, but based on literature findings, decided*  
164 *it would not have made a major difference on results.*

165 256: Did you not measure soil water isotopes directly ? What is the uncertainty of the model  
166 approach?

167 *Soil water isotopes were measured, as presented in section 2.2.5.*

168 *The uncertainty of the model approach is governed by the uncertainty of the chamber measurements*  
169 *of ET isotopic compositions and the parameterisation of Craig-Gordon (GG) model. While it is*  
170 *difficult to assess the accuracy of the CG model without direct observations, we did try different*  
171 *parameterisations (i.e. using Cappa et al (2003) vs Merlivat (1978) diffusion coefficients, and*  
172 *different values for the diffusion exponent). This had a large effect compared to uncertainty in ET*  
173 *isotopic compositions, but does not change the interpretation that soil water at the evaporation front*  
174 *was very enriched with very low D-excess values. While assessment of the CG model was not our*  
175 *focus, we can certainly provide some mention of the uncertainty of the model and how this may*  
176 *impact upon our results/interpretations in the discussion of water pool isotopic compositions (results*  
177 *section 3.2).*

178

179 **References**

- 180 Aemisegger, F., Pfahl, S., Sodemann, H., Lehner, I., Seneviratne, S. I. and Wernli, H.: Deuterium  
181 excess as a proxy for continental moisture recycling and plant transpiration, *Atmos. Chem. Phys.*,  
182 14(8), 4029–4054, doi:10.5194/acp-14-4029-2014, 2014.
- 183 Bastrikov, V., Steen-Larsen, H. C., Masson-Delmotte, V., Griбанov, K., Cattani, O., Jouzel, J. and  
184 Zakharov, V.: Continuous measurements of atmospheric water vapour isotopes in western Siberia  
185 (Kourovka), *Atmos. Meas. Tech.*, 7(6), 1763–1776, doi:10.5194/amt-7-1763-2014, 2014.
- 186 Cappa, C. D., Hendricks, M. B., DePaolo, D. J. and Cohen, R. C.: Isotopic fractionation of water  
187 during evaporation, *J. Geophys. Res. Atmos.*, 108(D16), 4525, doi:10.1029/2003JD003597, 2003.
- 188 Lu, X., Liang, L. L., Wang, L., Jenerette, G. D., McCabe, M. F. and Grantz, D. A.: Partitioning of  
189 evapotranspiration using a stable isotope technique in an arid and high temperature agricultural  
190 production system, *Agric. Water Manag.*, In Press, ,  
191 doi:http://dx.doi.org/10.1016/j.agwat.2016.08.012, 2016.
- 192 Merlivat, L.: Molecular diffusivities of H<sub>2</sub>O<sup>16</sup>O, HD<sup>16</sup>O, and H<sub>2</sub><sup>18</sup>O in gases, *J. Chem. Phys.*,  
193 69(6), 2864, doi:10.1063/1.436884, 1978.
- 194 Risi, C., Noone, D., Frankenberg, C. and Worden, J.: Role of continental recycling in intraseasonal  
195 variations of continental moisture as deduced from model simulations and water vapor isotopic  
196 measurements, *Water Resour. Res.*, 49(7), 4136–4156, doi:10.1002/wrcr.20312, 2013.
- 197 Simonin, K. A., Link, P., Rempe, D., Miller, S., Oshun, J., Bode, C., Dietrich, W. E., Fung, I. and  
198 Dawson, T. E.: Vegetation induced changes in the stable isotope composition of near surface  
199 humidity, *Ecohydrology*, 7(3), 936–949, doi:10.1002/eco.1420, 2014.
- 200 Wang, L., Niu, S., Good, S. P., Soderberg, K., McCabe, M. F., Sherry, R. A., Luo, Y., Zhou, X., Xia,  
201 J. and Caylor, K. K.: The effect of warming on grassland evapotranspiration partitioning using laser-  
202 based isotope monitoring techniques, *Geochim. Cosmochim. Acta*, 111, 28–38,  
203 doi:http://dx.doi.org/10.1016/j.gca.2012.12.047, 2013.
- 204 Welp, L. R., Lee, X., Griffis, T. J., Wen, X.-F., Xiao, W., Li, S., Sun, X., Hu, Z., Val Martin, M. and  
205 Huang, J.: A meta-analysis of water vapor deuterium-excess in the midlatitude atmospheric surface  
206 layer, *Global Biogeochem. Cycles*, 26(3), GB3021, doi:10.1029/2011GB004246, 2012.
- 207 Zhao, L., Wang, L., Liu, X., Xiao, H., Ruan, Y. and Zhou, M.: The patterns and implications of  
208 diurnal variations in the d-excess of plant water, shallow soil water and air moisture, *Hydrol. Earth  
209 Syst. Sci.*, 18(10), 4129–4151, doi:10.5194/hess-18-4129-2014, 2014.