

Review of

“Deuterium excess in atmospheric water vapor of a Mediterranean coastal wetland: regional versus local signatures”

by Delattre, et al.

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1 General Comments

This paper presents very valuable high temporal resolution water vapour isotope measurements in an interesting setting close to Vaccarès Lagoon in southern France. Thirty six consecutive days of hourly $\delta_v^{18}\text{O}$, $\delta_v^2\text{H}$ and deuterium excess (d_v) measurements in atmospheric water vapour from the summer 2011 are used to investigate the relative importance of local and regional processes. The relevant local process is thought to be evaporationspiration. “Remote” processes encompass all the large scale atmospheric properties that determine the background isotope signature of water vapour. The measured isotope data is compared to local atmospheric measurements of temperature, specific and relative humidity. Furthermore, a simple backward trajectory analysis is applied to characterise the dominant atmospheric flow situation and a two component isotope mixing model is used to quantify the contribution of local evapotranspiration to the increase in measured boundary layer water vapour mixing ratio during the day.

Relevant aspects with respect to the interpretation of water vapour isotopes in continental near-surface ambient air and the possible mechanisms behind the measured signals are discussed in this paper. However, I have several major comments that I think the authors should address:

1. **Data quality:** The accuracy and precision values indicated in Table 3 suggest an unrealistically low total uncertainty for water vapour measurements with a Picarro instrument of the L1102 series. This is partly due to the fact that liquid water measurements are used for calibration and for precision and accuracy indications. Please provide a more adequate uncertainty estimation of your water vapour measurements. The uncertainty in the composition of the standards (Table 1) used for calibration is much larger than the indicated accuracy and precision values. This should be taken into account (see also specific comment on Table 3).
2. **Local vs “remote” signatures:** The authors try to isolate the respective influence of local and remote processes on their measured isotope signals in continental water vapour. This is indeed an important research question. However there are several instances in the paper, where the reader gets confused in the argumentation line of which processes (local or remote) is thought to be dominant at which time-scale (see specific comments below). This is an important caveat of this paper. Maybe this confusion comes from the fact that the dominant process is most probably not the same for the daily (section 4.1) and the sub-daily time-scale (section 4.2) ?
3. **Water and isotopic mass budget of the boundary layer:** The motivation, the applicability and the implementation of the two end-member mixing model is my biggest concern in this paper. An effort should be made by the authors to explain what the exact purpose of using their simple mixing model is, what the assumptions are behind and discuss their results critically:
 - a) **Motivation:** the structure of the paper makes it difficult for the reader to understand why this mixing model is introduced at all. A clear motivation for such an approach is missing in the introduction. Since the used mixing model has been applied in a range of studies a short overview of these should already be given in the introduction, to better put this study into context. Furthermore, the content of Section 4.2.6, where the results from the mixing model are used, should directly follow the introduction of the mixing model in Section 4.2.3.
 - b) **Interpretation of the correlation between δ_v and q :** In several instances in the paper the authors say that a good correlation between δ_v and q is an indication for air mass mixing and use this as an argument for applying their two end member mixing model. But wouldn't the correlation between δ_v and q be high as well, if we had only one water vapour source, because of the progressive (Rayleigh-type) rain out during transport? Of course, the water vapour, in which isotopes were measured here has many different moisture sources and has been affected by air mass mixing, but why is it the good correlation between δ_v and q that tells you this?

- c) **Assumptions:** The simple two end-member mixing model used for determining the surface vapour flux composition (“composition of the vapour source”) is based on very strong assumptions, which are not clearly stated in the manuscript. To me the measurement setting would suggest a mixing of (at least) three rather than two main water vapour sources with distinct isotope signatures: evaporation from the lagoon, local evapotranspiration and “remote” moisture that is mixed into the boundary layer by entrainment during the day.
- d) **Physical meaning of the obtained isotope composition of the end members:** If I understood it correctly the obtained “surface vapour compositions” actually represent an estimation of the isotopic signature of the evapotranspiration flux. But these values are not further used or compared to any similar values in the literature. In the way this result is presented now, I am not convinced that these values have any physical meaning.
- e) **Confusing notation: mixing ratio vs “vapour flux“:** My difficulty in understanding why and how the two end-member mixing model is applied in this paper (probably) comes partly from the author’s notation that seems confusing to me: q stands for the water vapour mixing ratio in $\text{mmol}\cdot\text{mol}^{-1}$ in most parts of the paper, except in section 4.2.3 where it seems to represent a “vapour flux”. In Equation 5, $Q_{\text{ET}}/Q_{\text{BG}}$ is used, which seems to also represent a ratio of fluxes. Please use a more adequate notation and clearly differentiate between fluxes and mixing ratios.

2 Technical comments: structure and references

1. The writing could be much more concise and the structure has some weaknesses in the results part, particularly in Section 4.2 but also in Section 4.1.
2. Often only recent studies are referenced, please also cite the original literature (see specific comments below).
3. The references should be indicated in chronological order.
4. The abbreviations are not introduced and used consistently for example for evapotranspiration (ET).

3 Specific comments

1. p. 1704, l. 12: “At the daily time-scale would be less confusing.
2. p. 1704, l. 19: “Based on twenty-four average hourly data”. Do you mean the multi-day mean hourly data?
3. p. 1705, l. 12: replace “continental evapotranspiration” by “evapotranspiration”.
4. p. 1705, l. 12-16: “high continental evapotranspiration may contribute to regional rainfall in contexts of tropical rainforest ..., or may even reduce potential evapotranspiration.” I do not understand what this means, please rephrase.
5. p. 1706, l. 7: ~ 1 Hz is the current maximum time resolution of laser spectrometric measurements.
6. p. 1707, Introduction in general: there are many good reasons why studying the water cycle in the Mediterranean region is important. Please be specific why conducting a study like this is important in this region.
7. p. 1707, l. 8-11: see my main comment 3c, to me this implies more than two sources of moisture.
8. p. 1707, l. 14: “average hourly variations”, make it clear that you look at typical daily cycles.
9. p. 1708, l. 2: “avoid any fractionation” this is a very optimistic statement, “minimise wall effects that lead to fractionation in the inlet” would be more realistic, especially since you mention condensation problems on p. 1709, l. 10.
10. p. 1708, l. 22: “very nearly” replace by “nearly”.

11. p.1710, l.21: Generally, normalisation of water isotope measurements to the VSMOW2-SLAP2 scale is done following the IAEA Reference Sheet for International Measurement Standards http://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf.
12. p.1711, l.11: See major comment 1, please provide more adequate uncertainty estimates for your measurements.
13. p.1711, l.3: “Climatic” is maybe not the right term here, local atmospheric data or meteorological data would be more adequate.
14. p.1711, l.9: Shortly explain what you mean by “potential evapotranspiration“ and provide a reference for the Penman-Monteith equation (Monteith, 1965).
15. p.1712, l.2: Since you are looking at the day-to-day and sub-daily variations using the hourly data, it may be clearer to say “For $\delta^{18}\text{O}$ and $\delta^2\text{H}$ substantial day-to-day variations are observed, which appear higher than the sub-daily variations. For d_v , ...”. Since d_v is the main topic of this paper, I wouldn’t say “..., except for d_v ”. Is it by eye that you would say that the day-to-day variations in d_v are smaller than the sub-daily variations or is this a quantitative result?
16. p.1712, l.4: Title 4.1 “Time series analysis” is a bit unspecific.
17. p.1712, l.14: Cite the original literature here Dansgaard (1964).
18. p.1712, l.21: If you are referring to the study by Jacob and Sonntag (1991), I think their measurements were done in Heidelberg, Germany.
19. p.1712, l.23-27: I don’t understand why a good correlation between δ_v and q “suggests mixing between air masses”. See major comment 3b.
20. p.1713, l.10: “The significance of deuterium excess in terms of vapour sources”. Do you mean “in terms of a proxy for the conditions at the moisture sources” ?
21. p.1713, l.25: “However, relative humidity combines both temperature and water concentrations, and q , which purely reflects the amount of water, can better describe an air mass”. I find this sentence very confusing. q represents the water vapour mixing ratio, right?
22. p.1713, l.25-28: I don’t understand your argument here. See again major comment 3.
23. p.1714, l.1: The section title 4.1.2 could be more precise.
24. p.1714, l.21: Since the paper is a quite long and you do not have many precipitation samples, I wonder, whether this section is really necessary.
25. p.1716, l.18: I would not say that the vapour measurements presented here are particularly depleted. Isn’t the lower $\delta^2\text{H}$ - $\delta^{18}\text{O}$ slope rather due to evapotranspiration (local and regional). See Gibson, et al. (2008).
26. p.1716, l.22: I find “average daily variations” confusing here, maybe “average daily cycles” would be better.
27. p.1716, l.24: I also find “24 h average values” confusing. You are computing 36 days averages to obtain an average hourly diurnal cycle. “Typical daily cycles” may be the best way to describe it.
28. p.1716, l.26: I would say “meteorological condition” not “climatic condition”.
29. p.1718, l.1: The section title for 4.2.2 should be “Sub-daily variations” or “Diurnal” otherwise it is confusing. ET has not yet been introduced as evapotranspiration
30. p.1718, l.5: “by free atmospheric air”.
31. p.1718, l.8: “surface sensible heat flux”.
32. p.1718, l.11: “entrainment of free atmospheric air”.
33. p.1718, l.14: also cite the earlier literature here, say (e.g., Dansgaard, 1964; Gat, 1996; Gonfiantini, et al., 2001).

34. p. 1718, l. 16: also cite Lai, C.-T., et al. (2006); Lai and Ehleringer (2011) here.
35. p. 1718, l. 13: You say “Both processes influence d_v in the same direction but not δ_v .” A priori I don’t see why.
36. p. 1718, l. 17-20: Confusing sentence. Isn’t the daily cycle of d_v influenced by both evapotranspiration and admixture of free tropospheric air?
37. p. 1718, l. 26-28: Confusing, I don’t understand the argumentation line here.
38. p. 1719, l. 10: see major comment 3.
39. p. 1719, l. 11: Replace “climatic” by “meteorological”.
40. p. 1719, l. 25: Equation 3 is very confusing to me since q seems to be used for water vapour mixing ratios before this section (see my major comment 3e).
41. p. 1720, l. 16-19: What do you mean by this? You nevertheless infer surface vapour compositions in the subsequent paragraph using the mixing model.
42. p. 1720, l. 20-27: I don’t understand what these “surface vapour” isotope compositions physically represent. Why are they so different in d_v (52‰ for “Atlantic conditions” and 36‰ for “Mediterranean conditions”). If these numbers should reflect the soil moisture or lagoon water isotopic composition, I don’t think it makes sense to cluster the days according to the dominating atmospheric large-scale weather situation, since the soil moisture isotopic composition changes consistently in time depending on the precipitation input and the evaporative enrichment.
43. p. 1720, l. 20-27: Do you have an idea about the isotopic composition of the pond water of the Vaccarès Lagoon?
44. p. 1720, l. 29: Units are missing.
45. p. 1720 l. 28 - p. 1721, l. 1-4: This is a very general statement and does not explain what these “surface vapour” isotope compositions really mean. To me your sentence “The contribution of ET has thus a huge effect on regional d_v ” somehow contradicts your approach of computing different daily cycles for different “air mass origins”. If ET is so important, why would the daily cycles be different for different large-scale conditions.
46. p. 1721, l. 17 & p. 1722, l. 5: What do you mean by “average composition of the atmosphere”? This is a bit unspecific. Averaged in time/space, over what region/vertical levels?
47. p. 1722, l. 7: Shouldn’t it be d_v -RH relationship, you don’t mention the individual δ_v -RH relations.
48. p. 1722, l. 15-22: I don’t agree with this statement. What do you mean by a “stationary state”? The d_v -RH relation (with RH at the moisture source at the time of evaporation) reflects a fundamental physical link established during evaporation due to the non-equilibrium fractionation.
49. p. 1723, l. 2, Equation 5: I do not understand the meaning of Q_{ET}/Q_{BG} and what the obtained values should reflect (see major comment 3)
50. p. 1723, l. 3, Equation 6: I do not understand this equation. PET is per definition larger than the actual ET, so with this equation you will overestimate the contribution of daily ET to the night-time background atmosphere.
51. p. 1724, l. 27: use d_v instead of deuterium excess.
52. p. 1725, l. 15: “We thus show that...” I would say that this is still only a hypothesis.
53. p. 1725, l. 15-17: I am not convinced by this. You show that the daily cycles look quite different in terms of amplitude and night-time background value, depending on the large-scale flow situation. Doesn’t this suggest that both local and remote moisture sources matter: Local ET determines the daily cycle structure (maximum around midday, night-time minimum) and the large-scale advection of moisture determines the free atmospheric-background and thus to a large extent the absolute isotope values?

54. Table 3: I find that the (average?) deviation of the mean of Standard 2 from its known value is not a good measure for the accuracy of the measurements (I am not sure that I really understood how you computed the accuracy, a root mean square error would be more adequate). Estimating the uncertainty of water vapour measurements using liquid injections generally leads to an underestimation of the measurement error. Aemisegger, et al. (2012) discuss the different uncertainty sources of water vapour isotope measurements using cavity ring-down laser spectrometers from Picarro.
55. Table 5: Mention that the indicated isotopic compositions are local values from Camargue. In the present form it is slightly confusing, the values could also indicate the isotopic composition of the water vapour at the moisture source (Atlantic, Mediterranean or Bay of Biscay).
56. Figure 2: different symbols could be used here for the different standards instead of the three colours that are already used for the air mass influence.

References

- Aemisegger, F., Sturm, P., Graf, P., Sodemann, H., Pfahl, S., Knohl, A., and Wernli, H.: Measuring variations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in atmospheric water vapor using two commercial laser-based spectrometers: an instrument characterisation study, *Atmos. Meas. Tech.*, **5**, 1491-1511, doi:10.5194/amt-5-1491-2012, 2012.
- Dansgaard, W.: Stable isotopes in precipitation, *Tellus*, **16**, 436-468, doi:10.1111/j.2153-3490.1964.tb00181.x, 1964.
- Gat, J.: Oxygen and hydrogen isotopes in the hydrological cycle, *Annu. Rev. Earth Planet. Sci.*, **24**, 225-262, doi:10.1146/annurev.earth.24.1.225, 1996.
- Gibson, J. J., Birks, S. J., and Edwards, T. W. D. : Global prediction of δ_A and $\delta^2\text{H}-\delta^{18}\text{O}$ evaporation slopes for lakes and soil water accounting for seasonality, *Tellus*, **16**, 436-468, doi:10.1111/j.2153-3490.1964.tb00181.x, 2008.
- Gonfiantini, R., Roche, M.-A., Olivry, J.-C., Fontes, J.-C., and Zuppi, G. M.: The altitude effect on the isotopic composition of tropical rains, *Chemical Geology*, **181**, 147-167, doi:10.1016/S0009-2541(01)00279-0, 2001.
- Jacob, H. and Sonntag, C.: An 8-year record of the seasonal variation of ^2H and ^{18}O in atmospheric water vapor and precipitation at Heidelberg, Germany, *Tellus*, **43B**, 291-300, doi:10.1034/j.1600-0889.1991.t01-2-00003.x, 1991.
- Lai, C.-T., Ehleringer, J. R., Bond, B. J., and Paw U, K. T.: Contributions of evaporation, isotopic non-steady state transpiration and atmospheric mixing on the $\delta^{18}\text{O}$ of water vapour in Pacific Northwest coniferous forests, *Plant, Cell Environ.*, **29**, 77-94, doi:10.1111/j.1365-3040.2005.01402.x, 2006.
- Lai, C.-T. and Ehleringer, J. R.: Deuterium excess reveals diurnal sources of water vapor in forest air, *Oecologia*, **165**, 213-223, doi:10.1007/s00442-010-1721-2, 2011.
- Monteith, J. L.: Evaporation and environment, *Symposia of the Society for Experimental Biology*, **19**, 205-224, 1965.