

## Revision of the manuscript:

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

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## General responses:

*(all the responses from the authors are in blue)*

We are very grateful to all the reviewers for their detailed and constructive comments. Following the recommendations of all reviewers, we have modified and simplified the structure of the manuscript, in order to clarify the evidences of regional and local influences. The structure of the “results and discussion” part is now as follows:

#### 4.1 Correlations between isotope data and climatic parameters

In this section, we have kept the comparison between statistical correlations, leading to evidence of mixing processes between different air masses (previous #4.1.1 “correlation between isotope data and climatic parameters ...”), but we have better described correlations between the deuterium excess and relative humidity (RH) which was previously discussed in a separate section (previous #4.2.5). We have also added in Table 4 and 5 a comparison between results obtained with RH reported to air temperatures (RH<sub>a</sub>) and reported to water surface temperature (RH<sub>s</sub>). This helps to clarify that the mixing ratio (q) is a better predictor of isotopic variations than relative humidity in our case.

#### 4.2 Regional isotopic signatures

In this section, we have joined the two previous sections called “4.1.2 influence of backward trajectories” and “4.1.4  $\delta^{18}\text{O}$ - $\delta\text{D}$  relationships”. This helps to better focus on the clear differences in  $\delta_v$  relative to the regional influences. In addition, we have removed the section “4.1.3 comparison with rainfall composition”, following the recommendation of referee #2, and discuss our scarce rainfall data more concisely.

#### 4.3 Analysis of average daily cycles

Here we describe the typical diurnal cycles displayed in Figure 5 (previous #4.2.1 “Average daily cycles relative to air mass origins”), and argue for the influence of surface evaporation during day-time (previous # 4.2.2 “Daily variations of  $\delta_v$  controlled by surface ET”), and for the imprint of dew formation during the night.

#### 4.4 Local isotopic signatures

Finally we propose a quantitative interpretation of diurnal mixing processes, starting with the determination of the local vapor pool composition based on a two-component mixing model (previous #4.2.3 “Composition of surface vapor influx”). We

then apply an isotopic mass balance in order to estimate the contribution of this local vapor to the ambient moisture for the two main meteorological conditions, and discuss the validity of the two-component mixing assumption. We end up the discussion by proposing a qualitative interpretation of the typical diurnal isotopic variations based on the  $\delta^{18}\text{O}$ - $\delta\text{D}$  relationships (previous # 4.2.4 “ $\delta^{18}\text{O}$ - $\delta\text{D}$  relationships”).

We have thus significantly simplified the previous #4.2.6 “PBL water budget”, and only kept a qualitative comparison of the influence of regional advection under North Atlantic meteorological conditions.

We have also mostly focus on local evaporation, instead of “evapotranspiration”, since the environment of our experimental site is evidently dominated by evaporation, upon transpiration.

## **Responses to comments from referee #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  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and deuterium excess (d) 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 evapotranspiration. “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).

We have modified Table 1 and 3 in order to better explain how is the performance of our measurements estimated.

Table 1 shows the composition of our liquid working standards calibrated with IAEA primary standards, and statistics on raw measurements of these working standards during the field campaign, as an estimate of instrument stability. It has been made clearer in the title.

Table 3 displays the results of Standard 2 measurements ( $\delta_{std2-m}$ ) normalized to the VSMOW2-SLAP2 scale by using Standards 1 and 3 as working standards. Standard deviation provides the reproducibility, and we have added the root mean square deviation from the known value (RMSE) to estimate the accuracy of liquid measurements.

We have thus modified the accuracy estimation, as suggested by the referee, and used the RMSE instead of the difference between average calibrated values and known value (0,03‰ and 0,1‰ for  $\delta^{18}O$  and  $\delta D$  respectively). The similarity between standard deviation and RMSE indicates that there is almost no bias, and that the measurement accuracy is mostly limited by the reproducibility.

All these performance evaluations are based on liquid measurements, and we agree that uncertainties on vapor measurement are probably higher. We have added the following sentence in section #2.3: *“These performances are estimated on liquid measurements, and are probably lower for vapor measurements.”*

**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) ?

We have modified the structure of the manuscript, in order to clarify the respective influences of regional and local processes with respect to the corresponding time-scales (see our general responses). We agree that the terms “remote” and “regional” vapor was not clear enough, and we have removed the “remote” term, in order to be consistent with the local/regional discussion.

**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.

The motivation of this approach is now better explained in the abstract:

*“Based on a two-component mixing assumption, we calculate the average composition of the local vapor source that produces the day-time increase in  $\delta v$ , and estimated the contribution of this local vapor to the ambient moisture. Amplitudes and ranges of diurnal variations in  $\delta v$  and  $\delta v$  are compared for the different regional meteorological situations, and the influence of regional advection is discussed. This isotopic mass balance approach is proposed as a framework for deciphering regional and local influences.”*

And also in the introduction:

*“We will focus on identifying the main drivers of deuterium excess variability at different time scales, and explore the relevance of using either relative humidity, as an indicator of evaporation conditions, or specific humidity (mixing ratio) as a proxy of mixing between different vapor sources”*

In the revised manuscript we have reduced the importance given to the water and isotopic mass budgets of the PBL. The mixing model is thus not described in the introduction, but in the section #4.4. This approach is proposed as a framework for analysing mixing processes.

b) Interpretation of the correlation between  $\delta v$  and  $q$ : In several instances in the paper the authors say that a good correlation between  $\delta v$  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  $\delta v$  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  $\delta v$  and  $q$  that tells you this?

We agree that there is also a  $\delta v$ - $q$  correlation in the case of a Rayleigh process, but we argue that the  $\delta v$ - $q$  correlation is an indication of mixing processes in our case, because:

- at daily time step: 1) the  $\delta v$ - $q$  correlation is better than the  $\delta v$ - $T$  correlation and 2) there is also a good correlation between  $\delta v$  and  $q$  ( $\delta v$  being almost conservative in the case of rain-out)
- at hourly time-step, the correlation used for applying the mixing model correspond to a  $q$ -increase period (while the Rayleigh-type process is observed during night-time, a  $q$ -decrease period)

We have clarified these points (in section # 4.1 and #4.3), and explained with more details the nocturnal dehydration process. We have also added a paragraph in the conclusion.

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.

We fully agree that the two-component mixing model is probably oversimplified. We propose this approach as a framework of deciphering the local and regional influences, and we have added a more detailed discussion of the validity of the assumption behind the model, specifically the influence of advection (see section #4.4)

Concerning the possible influence of transpiration, considering the availability of open water around the site, the local vapor component is largely dominated by evaporation. We have added a discussion of the composition found for the local vapor. The local vapor pool corresponds to an average value that encompasses all the different local vapor sources (see the following point), including transpiration, but the latter is largely dominated by evaporation.

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.

We have added a discussion of the composition found for the local vapor. The high deuterium excess is consistent with a local vapor produced by open water evaporation (i.e. Gat et al 1994 found  $\delta D$  values between 34 and 88 ‰)

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,  $Q_{ET}/Q_{BG}$  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.

We have clarified the notation, keeping  $q$  for mixing ratios only (absolute vapor concentrations), and using  $W$  in equations 3 and 7 for referring to absolute vapor

quantity. We have removed fluxes terms, since the time dimension is in fact not necessary for the mass balance equations that we use.

### **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.

The manuscript structure is modified (see general comments)

2- Often only recent studies are referenced, please also cite the original literature (see specific comments below).

We have added original literature (Craig and Gordon, 1965, Dansgaard, 1964, Gat et Matsui, 1991, Gat et al, 1994, Gibson et al, 2008, IAEA, 2009, Monteith, 1965)

3- The references should be indicated in chronological order.

Modified

4- The abbreviations are not introduced and used consistently for example for evapotranspiration (ET).

Checked and corrected.

### **Specific comments**

1- p. 1704, l. 12: "At the daily time-scale would be less confusing.

corrected

2- p. 1704, l. 19: "Based on twenty-four average hourly data". Do you mean the multi-day mean hourly data?

Yes

3- p. 1705, l. 12: replace "continental evapotranspiration" by "evapotranspiration".

done

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.

We have added the following explanation:

*"High evapotranspiration [...] may reduce potential evapotranspiration by lowering temperature and increasing humidities near the earth surface"*

5- p. 1706, l. 7: ~1 Hz is the current maximum time resolution of laser spectrometric measurements.

Corrected in the text

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.

We have added a short paragraph in the introduction.

7- p. 1707, l. 8-11: see my main comment 3c, to me this implies more than two sources of moisture.

In the introduction, we now state: *“Our experimental site is located close to the main lagoon (the Vaccarès lagoon, 65 km<sup>2</sup>), and provides the opportunity to investigate how local evaporation combines and interact with the other regional vapor sources.”*

As explained in our general responses, we have more explicitly focused our discussion on local evaporation, instead of “evapotranspiration”. Regarding the environment of our experimental site, and the large surfaces of open water, evaporation flux largely dominates transpiration. This is also discussed in the section # 4.4.

8- p. 1707, l. 14: “average hourly variations”, make it clear that you look at typical daily cycles.

A sentence was added in the introduction, and we now more clearly state this objective.

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.

We agree and we have modified accordingly.

10- p. 1708, l. 22: “very nearly” replace by “nearly”.

done

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](http://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf).

Our results are normalized to the VSMOW2-SLAP2 scale by using a 3-point calibration, in order to check for the linearity of the calibration, in addition to the correction for the scale compression. The two-point calibration (following the IAEA reference sheet) was used to evaluate the performance of our instrument (see Table 3). This has been clarified in the text, and in Table 3.

12- p.1711, l.11: See major comment 1, please provide more adequate uncertainty estimates for your measurements.

See our responses to major comment 1.

13- p. 1711, l. 3: “Climatic” is maybe not the right term here, local atmospheric data or meteorological data would be more adequate.

We have replace “3- Climatic data” by “3- Local atmospheric data”

14- p. 1711, l. 9: Shortly explain what you mean by “potential evapotranspiration” and provide a reference for the Penman-Monteith equation (Monteith, 1965).

We have added the reference for the Penman-Monteith equation.

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?

We have slightly modified the sentence according to this comment. This is not a quantitative statement, our aim is to introduce the need of a sub-daily analysis for interpreting  $d_v$  variability.

16- p. 1712, l. 4: Title 4.1 “Time series analysis” is a bit unspecific.

The general structure was changed (see general response)

17- p. 1712, l. 14: Cite the original literature here Dansgaard (1964).

Done

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.

Yes of course, it was in Germany. We have corrected this mistake.

19- p.1712, l.23-27: I don’t understand why a good correlation between  $\delta v$  and  $q$  “suggests mixing between air masses”. See major comment 3b.

See our responses to 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” ?

Yes, this is what we want to say. The modification was included.

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?

In the revised manuscript, we have explicitly added a discussion of the respective relevance of relative humidities reported to air ( $RH_a$ ) or surface temperatures ( $RH_s$ ). We have modified the sentence as follows (section #4.1):



*“However, relative humidity is only relevant for characterizing evaporation conditions if reported at surface temperature. In this case it represents the vapor concentration gradient between water and air, which controls the kinetic fractionation.”*

We have also added RH<sub>s</sub> values in table 4, 5 and in Figure 5.

22- p. 1713, l. 25-28: I don't understand your argument here. See again major comment 3.

Please refer to our response to major comment 3, and to previous comment. We have explicitly mentioned the bad dv-RHs correlation in section #4.1, and, hopefully, better argued for the relevance of dv-q correlations in terms of mixing between different vapor sources.

23- p. 1714, l. 1: The section title 4.1.2 could be more precise.

The section title is now “Regional isotopic signatures” (see our general responses)

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.

We have removed this section (as was also suggested by reviewer #2), and only kept a short description of rainfall compositions in the beginning of section #4.

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).

We agree, and we have added the following sentence: *“The previously described shift in dv during Rayleigh-type rainout, due to the non-linearity in the deuterium excess definition, is not sufficient for explaining these low slopes, and non-equilibrium processes such as evaporation are also probably involved (Gibson et al., 2008).”*

26- p. 1716, l. 22: I find “average daily variations” confusing here, maybe “average daily cycles” would be better.

Agreed (see title of section #4.3)

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.

OK, corrected

28- p. 1716, l. 26: I would say “meteorological condition” not “climatic condition”.

OK, it has been corrected here and elsewhere in the text, when it was relevant.

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

[This section title has been removed \(see the new structure of the manuscript\)](#)

30- p. 1718, l. 5: “by free atmospheric air”.

[corrected](#)

31. p. 1718, l. 8: “surface sensible heat flux”.

[The text has been made more concise, and this sentence was removed.](#)

32- p. 1718, l. 11: “entrainment of free atmospheric air”.

[Corrected](#)

33- p. 1718, l. 14: also cite the earlier literature here, say (e.g., Dansgaard, 1964; Gat, 1996; Gonfiantini, et al., 2001).

[Pioneer literature has been added in several part of the manuscript.](#)

34- p. 1718, l. 16: also cite Lai, C.-T., et al. (2006); Lai and Ehleringer (2011) here.

[done](#)

35- p.1718, l.13: You say “Both processes influence  $dv$  in the same direction but not  $\delta v$ .” A priori I don’t see why.

[This has been more clearly argued. See the new version of paragraph “Day-time processes: contribution of local evaporation” in section 4.3](#)

36- p. 1718, l. 17-20: Confusing sentence. Isn’t the daily cycle of  $dv$  influenced by both evapotranspiration and admixture of free tropospheric air?

[Same response as #35](#)

37- p. 1718, l. 26-28: Confusing, I don’t understand the argumentation line here.

[Same response as #35](#)

38- p. 1719, l. 10: see major comment 3.

[See our general responses and our responses to major comment 3](#)

39- p. 1719, l. 11: Replace “climatic” by “meteorological”.

[done](#)

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).

[We agree and we have modified the symbols in equation 3 \(see our responses to major comment 3e\).](#)

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.

The use of the mixing model is now better explained (see section 4.4)

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.

We have added a discussion of the obtained isotopic composition:

*"Such high values are consistent with the isotopic composition of open water evaporation estimated from the Craig and Gordon model (Craig and Gordon, 1965; Gat et al, 1994), which have made it possible to detect the contribution of local vapor to regional precipitation (Gat et Matsui, 1991, Gat et al, 1994) or to partition the composition of a vapor flux into evaporation and transpiration (Williams et al., 2004). In our case, these high  $d_v$  values confirm that evaporation is largely dominant upon transpiration, and the higher  $d_v$  under North Atlantic air mass conditions is consistent with lower RHs, compared to Mediterranean conditions (Figure 5, Table 5)."*

In addition, we have also estimated the uncertainty associated with the obtained composition of  $\delta_E$ , and we now discuss explicitly the errors induced by the two-component assumption.

The clustering of days according to meteorological situations aims at providing an average picture of mixing processes, and during this period with very low rainfall, the surface water composition does not change substantially compared to the uncertainties associated with the end-member composition.

43- p.1720, l.20-27: Do you have an idea about the isotopic composition of the pond water of the Vaccarès Lagoon?

Yes, but we have chosen to focus on identifying average mixing processes from vapor data only. The water isotopic compositions span a relatively large range of enriched compositions (around  $\delta^{18}O = 0\text{‰}$  and  $\delta D = -10\text{‰}$  for the main lagoon water), consistent with the obtained values of  $\delta_E$ , but it will be another subject of discussion.

44- p. 1720, l. 29: Units are missing.

Corrected

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.

This sentence has been removed, and we have clarified the use of the mixing model approach, and the discussion of the results (see also our response to comment #42)

In brief, the night-time backgrounds are very different for the two meteorological situations, but in both cases, day-time values point towards a strong increase in  $\delta v$ .

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?

We have clarified as follows:

*“The averaged composition of the planetary boundary layer is thus represented by the value measured just after the sunset (20h UTC), when the PBL vanishes and produces a vertical mixing of the atmosphere”*

47- p.1722, l.7: Shouldn't it be  $\delta v$ -RH relationship, you don't mention the individual  $\delta v$ -RH relations.

Yes.

Anyway, this section has been removed in the new structure. See also our response to the comment #21.

We have also added the following paragraph in the conclusion:

*“Overall, our data showed that mixing ratio is a better predictor of deuterium excess variations than relative humidity, at both daily and sub-daily time scales, because mixing processes between different vapor sources have weakened the relevance of relative humidity as an indicator of evaporation conditions. At the daily time step, mixing ratio is a proxy of the air mass origin, since there is a huge contrast between Northern and Mediterranean air masses. At the sub-daily time step, the  $\delta v$ - $q$  correlation observed during the  $q$ -increase period results from the addition of local evaporation.”*

48- p. 1722, l. 15-22: I don't agree with this statement. What do you mean by a “stationary state”? The  $\delta v$ -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.

See our response to comment #47

49- p.1723, l.2, Equation 5: I do not understand the meaning of QET/QBG and what the obtained values should reflect (see major comment 3)

See our response to major comment 3. We now introduce the above mentioned equation (now equation #7) as follows:

*“As a first attempt, we use this  $\delta E$  composition for interpreting the diurnal amplitude of  $\delta v$  from a simple isotopic mass balance”*

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.

We used PET as a rough estimate of AET in wetlands.

However, this equation has been removed in the new version, and the results of the mixing model is now discussed in a more qualitative way (see our general responses, and our responses to major comment

51- p. 1724, l. 27: use  $\delta D$  instead of deuterium excess.

Done

52- p. 1725, l. 15: "We thus show that..." I would say that this is still only a hypothesis.

The conclusion has been rewritten.

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?

We agree. The conclusion has been rewritten in this sense.

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.

We have estimated the RMSE in Table 3. See our responses to major comment 1.

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).

Done

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.

Done.

## 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.
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## Responses to comments from referee #2

In this manuscript, Delattre and coauthors present measurements of the isotopic composition of water vapor from a near-coastal site in France and discuss the daily and subdaily variability in terms of synoptic-scale air mass transport and contributions from local evaporation. In my opinion, this carefully compiled dataset can be very valuable for an analysis of the regional atmospheric water cycle and is certainly worth publishing. However, I have some doubts with respect to the proposed interpretation of the data, and in particular I think that the quantitative budget analysis employing the two-component mixing model is flawed, as outlined in more detail below. The presentation of the results is generally adequate, but in some parts the English writing is a bit unclear.

### Major comments:

1. I don't think the distinction made by the authors between the interpretation of daily and subdaily variations makes much sense. In particular, I do not believe that the daily variations in deuterium excess are mainly driven by variations in the isotopic composition of different advected air masses (as stated, e.g., in the conclusions). Such a connection cannot be deduced from the fact that different deuterium excess values have been measured during periods with transport from the Mediterranean or North Atlantic region. This can be explained by differences in local evaporation: North Atlantic air masses (as described by the authors) are relatively cold and dry, and are thus associated with strong evaporation with high deuterium excess from the local lagoon, in contrast to the warmer and more humid Mediterranean air masses. I think this mechanism (and thus the effect of local-scale evaporation) can fully explain the measured differences in deuterium excess of ca. 5 permil. Accordingly, in my opinion both daily and subdaily variations of  $d$  are mainly driven by local evaporation conditions.

Nevertheless, this does not mean that deuterium excess loses the signature of its moisture source (page 1725, line 17). With the simple trajectory approach applied by the authors, the moisture sources of the sampled air masses can simply not be determined. In many cases, evaporation from the lagoon can be a very important local contribution (as also evident from the quantitative estimates presented in the second part of section 4.2.6). Via the mechanism described above, the local source conditions can drive the measured  $d$  variability, and the measurements are thus perfectly consistent with previous studies relating  $d$  to the relative humidity during evaporation (Craig and Gordon, 1965; Uemura et al, 2008; Pfahl and Wernli, 2008).

We have modified the structure of the paper, clarified the application of the two end-member mixing model, and better discussed the resulting compositions for the local vapor under the two main meteorological situations (see our general responses, and also our responses to reviewer #1). We have now explicitly discussed the difference in isotopic composition of local vapor ( $\delta E$ ) for the two main meteorological conditions (section #4.4).

We agree that there is a relation between higher  $\delta v$  in local vapor and lower relative humidity under Northern conditions. Nevertheless, the higher advection rates indicate that, under Northern conditions, the higher average value of measured  $\delta v$  results from the combination of both local evaporation and the signature of regional (remote) vapor.

We have added the following paragraph in section 4.4:

*“The stronger advection rate which prevails under North-Atlantic conditions and which smoothed the diurnal amplitude of variation, suggests that the higher average  $\delta v$  signature of water vapor (Table 5) results from the combined influences of higher  $\delta v$  in  $\delta E$  and in the regional vapor. Such high  $\delta v$  for North-Atlantic air masses can be explained by the longer continental trajectory. A more detailed mass balance including a quantification of advection fluxes would allow a more precise determination of the local evaporation composition, and would help to determine the composition of regional vapor”*

and in the conclusion:

*“Nevertheless, we found higher  $\delta v$  for the local vapor composition under North Atlantic air mass conditions consistent with lower humidity conditions. In addition, the stronger advection rate that prevails under North-Atlantic conditions suggests that, in this situation, the higher average  $\delta v$  of water vapor also reflects the signature of regional vapor.”*

In addition, we have better described in section 4.1 the correlations between the deuterium excess and relative humidity (RH) which was previously discussed in a separate section (previous #4.2.5). We have more explicitly discussed the respective relevance of relative humidities reported to air ( $RH_a$ ) or surface temperatures ( $RH_s$ ) and added values of  $RH_s$  in Table 4 and 5 and in Figure 5. This help to clarify that the mixing ratio ( $q$ ) is a better predictor of isotopic variations than relative humidity in our case.

2. The results from the isotope-based budget analysis in section 4.2.6 (smaller local contributions during North Atlantic compared to Mediterranean advection) do not make sense physically (one would expect larger evaporation into dryer North Atlantic air masses, as described above). The differences to the subsequent evaporation-based estimates are so large that they cannot just be argued away, rendering the quantitative results rather useless. I think the isotope-based analysis is flawed due to two reasons: First, if I am not mistaken there is an error in equation (5); instead of  $\delta v(\min)$ , there should be a  $\delta v(\max)$  in the denominator. Second (and probably even more important in a quantitative sense), I don't think that the end member for the background conditions during North Atlantic advection equals the value from the nighttime measurements.

First, we want to insist on the major changes that we have made in the revised version of the manuscript. We have simplified the interpretation of our mixing approach; and removed the section “PBL water budget”, and now make a more qualitative discussion of the amplitude of  $\delta v$  variations. The higher evaporation rates, which is apparently in



contradiction with lower diurnal variations under North-Atlantic conditions, shows that the strong advection has smoothed the diurnal variations. However, the isotopic mass balance (equation 7, previously #5) remains applicable, and the use of night-time background allows to interpret the diurnal amplitudes of  $\delta v$  variations.

As evident from Fig.5, in this case the PBL still has a certain extend during night, and the relative humidity is well below 100%, both pointing to a contribution of local evaporation also during nighttime. A dryer and more depleted end member would increase the nominator in equation 5 and thus yield a larger local contribution.

We agree, but the behaviour of night-time isotopic compositions indicate the occurrence of dew formation. Dew formation may be a very local process, which does not fully exclude the possibility of nocturnal evaporation from the lagoon (although a minor proportion of daily evaporation). In addition, as the condensation lead to deplete the vapor, the night-time back-ground at the end of the night is most probably the most depleted vapor, compared to other regional pools.

More generally, we hope that the rewriting of our mixing approach (explained in details above) would have made our approach more convincing.

#### **Minor comments:**

The notion "twenty-four average hourly data" applied for the daily cycle analysis (e.g. in the abstract, but also throughout the paper) is very confusing.

We have clarified, by announcing a daily cycle analysis

P 1704, L 22: "entrainment of free atmosphere" is awkward; I also think that this issue has only been treated in a very implicit way and should thus not be mentioned in the abstract.

It has been removed from the abstract

P 1705, L 25 ff: Isotope-enabled models are used for various studies, not only of land-atmosphere interaction. The number of references could be greatly reduced, as modeling does not play any role for this study.

OK, we have only kept four references.

P 1706: Another study presenting high-resolution isotope measurements from Europe is Iannono et al. (2010).

We have added the reference

P 1711: If possible, please provide references for the HYSPLIT model and GDAS dataset. The wording "parameterized to end up" is unclear (probably you have just started the trajectories there and performed the calculation backwards in time).

Yes

Furthermore, such simple trajectory calculations cannot be used to "get the oceanic source" of moisture, for which there are much more sophisticated methods (e.g. as used in Pfahl and Wernli, 2008). Please be more specific on how you perform the source corridor attribution of the air masses.

We have added a sentence for describing the HYSPLIT model:

*"The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is a complete system which allows computing simple air parcel trajectories."*

Our objective was essentially to identify the main meteorological situations that prevails in the study area, and to classify the data accordingly.

P 1712: Jacob and Sonntag (1991) used data from Heidelberg, Germany.

The mistake has been corrected.

P 1713, L 19 ff: I don't think that this is the reasoning of Welp et al.; they just argue that a correlation between  $d$  and locally measured RH implies local moisture sources. As noted before, RH at the moisture source, not as an "air mass property", is important for  $d$  variability.

We have clarified in section 4.1 the discussion of RH and  $q$  as driving factors of our isotopic variations (see our responses above).

Section 4.1.2: As noted before, simply calculating backward trajectories is not enough to determine moisture sources. Nevertheless, the trajectory analysis is useful for determining the prevailing air mass advection that can (as demonstrated by the authors), e.g., affect local relative humidity and surface evaporation. This should be made clearer, also in connection to Table 5 (where it should be clearly stated that the parameters represent local conditions during the advection of specific air masses, and not the conditions at the moisture source).

This has been clarified in Table 5, and in the new version of the manuscript.

P 1714, L 17: I don't think that rainout necessarily occurs along these trajectories. Already climatologically, the vapor from northerly air masses is more depleted.

The Northern meteorological situation in our study area often corresponds to atmospheric perturbations in the Northern regions, and it probably contributes to large ( $\sim 2,5\%$ ) difference in  $\delta^{18}O$ . However, we agree that there is also a climatological explanation (sea surface temperature and composition differences).

Section 4.1.3: The very scarce rainfall measurements do not contribute a lot to the merit of this study. In particular, I cannot identify any temporal trend from these data (cf. P 1715, L 15). The point that precipitation  $d$  is lower than  $d$  in vapor could also be made in one sentence.

We agree and we have removed the section "4.1.3 comparison with rainfall composition", and discuss our scarce rainfall data more concisely.

P 1717, L 7: Why should this transition always happen in the evening? May this also reflect variations in the timing of the PBL evening transition?

We agree, and have modified the sentence.

P 1717, L12-13: I don't understand this sentence. Does "subsequently" imply a temporal relationship?

This has been rewritten and clarified

P 1717: I think the differences in PBL heights between North Atlantic and Mediterranean advection are mainly related to the vertical temperature structure: Northerly advection transports a relatively cold air mass over a warmer surface, leading to a weaker stratification (and the other way around).

We agree and have added modified a sentence in section 4.3.

P 1718, L 6: "... do not directly depend on climatic factors": I don't understand this.

This has been rewritten and clarified

P 1718, L 13: Why should these processes affect d in the same way?

This has been rewritten and clarified

Sections 4.2.3 and 4.2.6: The notation with respect to  $q/Q$  is very confusing. Does  $q$  represent a mixing ratio or a flux (as stated on page 1719)? What is the difference between  $q$  and  $Q$ ?

This has been rewritten and clarified (see also our responses to major comment 3E from referee #1)

Section 4.2.3: The determination of the end member ("surface conditions") in the mixing model uses a linear relationship to estimate isotope values far away from the humidity range in which data are available (see Fig 6). Such a procedure is associated with substantial uncertainties, which should definitely be quantified (by taking into account the uncertainties of the linear regression). I suppose that this yields large error bars particularly for deuterium excess.

We have estimated the uncertainties, and we have better discussed the obtained values.

P 1722, L 1-6: This passage is particularly difficult to understand.

The interpretation of the  $\delta^{18}\text{O}$ - $\delta\text{D}$  plot has been rewritten in section 4.4.

#### References:

Craig, H., and L. I. Gordon (1965), Deuterium and oxygen 18 variations in the ocean and the marine atmosphere, in Stable Isotopes in Oceanographic Studies and Paleotemperatures, edited by E. Tongiorgi, pp. 9-130, Lab. Geol. Nucl., Pisa, Italy.

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feedback cavity enhanced absorption laser spectrometer, *J. Geophys. Res.*, 115, D10111, doi:10.1029/2009JD012895.

Pfahl, S. and Wernli, H.(2008): Air parcel trajectory analysis of stable isotopes in water vapor in the eastern Mediterranean, *J. Geophys. Res.*, 113, D20104, doi:10.1029/2008JD009839.

Uemura, R., Matsui, Y., Yoshimura, K., Motoyama, H., and Yoshida, N. (2008): Evidence of deuterium excess in water vapor as an indicator of ocean surface conditions, *J. Geophys. Res.*, 113, D19114, doi:10.1029/2008JD010209, 2008.

### **Responses to comments from referee #3**

The authors describe the calibration of a laser method to collect and analyze the isotopic composition of near surface water vapour, and then to interpret the measured record over a month to understand the significance of the data. The analytical protocols, data collection and calibration are well described. I believe the authors could have compared and contrasted their results with those provided by Kurita et al. (Atmos. Meas. Tech., 5, 2069-2080, 2012). He used a different brand of machine but provided data from another European city - Vienna.

The second, and major part of the manuscript (Section 4) attempts to provide an interpretation of the measured vapour isotope values. The data indicate several interesting features - higher d-excess which they attribute to northern rather than southern air mass; day vs night time variation - which should lead to a much clearer discussion and result that contributes to the objective laid out in the introduction. As is, after reading a lengthy discussion, the reader does not get a clear picture as to what the authors think is the cause of observed variability. I think that the day/night variability perhaps indicates something that is contrary to the simple vapour mixing scenario that they started with. If the authors do not believe that more can be said, the material they have now perhaps could be rewritten more concisely.

[We believe that the new structure of the manuscript, and the rewriting of the isotopic mass balance and discussion should have respond to the concern raised by reviewer #3. We have also cited Kurita et al. \(2012\).](#)