

Second revision of the manuscript:

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

by Delattre H, Vallet-Coulomb C., and Sonzogni C.

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(Responses from the authors in blue)

In this new version of the manuscript, the main changes are 1) an improvement of the abstract and the conclusion in order to better evidence that both regional and local signatures are recorded in our data; 2) a more detailed discussion of the two end-member mixing assumption, with a more precise description of sensitivity analysis performed to evaluate the impact of regional advection on the determination of δ_E ; and 3) a removal of equation 7, following the recommendation of referee #1.

We have improved the English writing, but let us know if a ACP copyediting remains necessary.

We have also checked all the detailed comments.

The annotated revised version of the text is provided below.

Report #1

1 General Comments

In the revised version of their paper, the authors have substantially improved the structure as well as the introduction and use of the two end-member mixing model. However, in my opinion, two important contradictory points remain to be clarified before final publication.

- 1. Simple isotopic mass balance to explain the diurnal amplitude of δ_v :** I am not sure that I understand Equation 7. I am not convinced that this is a valid approach to compute the contribution of local evaporation to the “background vapour”. The diurnal amplitude of δ_v is also strongly influenced by entrainment as discussed by the authors in L. 372-393 and L.478-487. What does W_E represent? What is the timescale over which this mass balance is computed? Is this a mass balance for the boundary layer? The mass balance should be introduced more carefully, otherwise it should be removed.

There is a lower proportion of locally evaporated vapour in ambient moisture under Northern conditions despite higher evaporation rates, compared to the Mediterranean situation. The mass balance (eq. 7) was provided in order to point this contradiction, due to the higher advection rate under northern conditions. Finally, we agree that it is not essential to keep this calculation, since the point can be made qualitatively. We have thus removed this paragraph, and put a greater focus on the impact of regional

advection on the two-component mixing assumption (see the response to referee #2 relative to the sensitivity analysis)

2. **Local vs “regional” moisture sources:** With their methodological approach, the authors can only characterise the local evaporation conditions. I think the discussion about the differences in local evaporation conditions depending on the large scale meteorological situation is interesting and the focus of the paper should be kept there. There are still several instances, where the reader gets confused in terms of what the authors argue to be the driving factor(s) behind the observed isotope signals (“local or regional signature”). Particularly the abstract and the conclusions should be improved in this sense.

We have modified the abstract and the conclusion, in order to clarify these points. In our opinion, our data record both local and regional signatures. The different meteorological situations associated to air mass back trajectories control both local evaporation conditions (determining δ_E), and the isotopic composition of regional advection.

2 Specific comments

1. p.2, L.11: “Stable isotopes of water vapour”, remove “the”.

Done

2. p. 2, L. 17: Replace evapotranspiration by evaporation.

Done

3. p. 2, L. 17-18: “A calibration protocol...” this sentence should be removed. This technical aspect is not the main topic of the paper.

Done

4. p. 2, L. 38: Replace “local vapour” by “local evaporation” or else more clearly differentiate what is meant by “local vapour” and “ambient moisture”.

We have clarified in the text, and replace “local vapour” by “locally evaporated vapour” when necessary.

5. p.4, L.74: Kurita et al. 2012 can be cited elsewhere (for example at L.80 or/and L. 96). Here citing the review by Kerstel and Gianfrani, 2008 would be more adequate.

Agreed, and modified.

6. p.7, L.175: Say “specific to the individual analyser” to avoid the repetition of “dependence”/ “dependent”. Here more than one study should be cited to give credit to this statement. Johnson et al., 2011 and Aemisegger et al., 2012 provide an in-depth discussion of this aspect for Picarro instruments. Furthermore since many recent studies discuss this aspect please write (e.g. Tremoy et al., 2011,...).

Corrected

7. p.9, L.247 What is D?

It designated “deuterium”, we have written it fully to avoid any confusion.

8. p. 10, L. 268 Say “plant transpiration”.

Done.

9. p. 9, L. 244 The precipitation deuterium excess data should also be shown in Figure 3.

Done.

10. p. 9, L. 255 The daily cycle of air and surface temperature should be added in Figure 5.

Done

11. p. 10, L. 295 Is it the $\delta v - T$ correlation that is meant?

We have clarified

12. p.13 L. 374 Lai and Ehleringer do not attribute the diurnal increase in d_v solely to entrainment of free atmospheric air. They use an explicit isotope mass balance to determine the importance of soil evaporation, plant transpiration and entrainment for the observed daily cycle in the water vapour isotopes.

We have modified the sentence.

13. p.13 L. 385 It should be Lai et al., 2006.

Corrected

14. p. 14, L. 396 I am not convinced that there is no evaporation from the lagoon during nighttime.

We agree, even if the surface fluxes (latent and sensible) are expected to remain minor during night-time. We have modified the sentence in this sense, and replaced « disappearance » by « reduction ».

15. p.15, L.428 I find the use of W_1 confusing here as well as in Equation 7 the use of W_E and W .

We have changed the symbol and corrected equation 3. Equation 7 has been removed.

16. p. 15, L. 447 It should be Noone et al., 2011, Noone, 2012.

Corrected

17. p. 18, L. 525-528. This is confusing. You say “Cold, dry and strong winds coming from the North bring an isotopically depleted vapour... from the South bring an isotopically enriched vapour”. This is not what I understood from the main text, in which you analyse the influence of local conditions on the isotope signals.

Later on, on L. 536-538 you say that it is local evaporation that mainly drives the daily isotope signals. This is contradictory (see also my general comment 2).

Our results show that local evaporation drives the intra-daily isotopic variations, while the differences in isotopic signal observed at a daily time step is mainly related to the air mass origins. We have clarified the conclusion and the abstract in this sense (see also our response to the general comment 2)

18. p. 18, L. 534 replace second "either" by "or". I don't agree with the "either... or..." statement. The relative importance of the two processes is different depending on daytime but both processes are equally relevant in shaping the typical daily cycle of water vapour isotope signals.

We have modified the sentence as follows : « *A diurnal increase in d can be caused by entrainment of free atmospheric air, by surface evaporation, or by a combination of both processes* »

Report #2

In this revision, Delattre et al. have improved their manuscript. Some points are still unclear, as detailed below, but once these have been clarified, I think the paper can be published in ACP. The English writing could still be improved (which can be done by the ACP copyediting, I believe).

Specific comments:

- Lines 28, 341, Figures 5-7: Here the term "24-hour average values" (or something similar) is still used for the daily cycle analysis, which is not correct (it indicates that the data have been averaged over 24 hours, which is not the case).

Corrected : we have replaced by « average daily cycles » or by « hourly average values over a daily cycle »

- L 33 and other places: The term "the PBL vanishes" is a bit strange; I think "collapses" would be better.

Corrected

- L 97-98: The abbreviations for d -excess should be harmonized.

We have replaced d_v by d to designate deuterium excess in the whole text

- L 225: "Backward trajectories were started/initialized" instead of "Trajectories were parameterized to end up"

Corrected

- L 227: It is still not clear what is meant by "oceanic source".

We have provided more details and clarified the text.

- L 274-295: The most important point here is not the normalization with respect to surface temperature, but the fact that it is the RH at the location where the water evaporated from the surface, and not at the measurement location, that is most closely related to the d-excess. As RH is not conserved during air mass transport (e.g., when the air parcel descends and is heated adiabatically, this changes RH), these are not the same. This should certainly be mentioned here.

We have clarified.

- L 306-308: It is still not very clear how this classification is done. Please be a bit more specific by explicitly mentioning the geographic limits/coordinates of the different sectors and the time (backward along the trajectories) for which the classification is performed.

We now refer to the more detailed explanation, which has been added in section 3.

- L 330 "strong linear fits are evidenced" is not correct English

We have replaced by « strong linear relationships are observed »

- L 396-412: It is a bit difficult to get the point of this paragraph, as the "dew formation" is only mentioned very late (in line 409). I'd note earlier that this is most likely the process leading to the observed gradual night-time depletion.

We have rewritten the paragraph.

- Page 15: It confuses me that the equations are given in two very similar forms with the same meaning, but different notations. Moreover, the units of the symbols in equation (3) do not match. I'd suggest to remove equations (3) and (4); all the physics can be explained with equations (5) and (6).

We agree and have corrected the mistake in equation (3). However, in our opinion, it is still interesting to provide both formulations (Eq. 3 and Eq. 5), since we want to clarify the proposed mixing approach and to compare it with the classical case (Keeling plot). In the case of the addition of « pure » water vapor in a humid air mass (equation 3), the amount of dry air (n_A) remains constant. The meaning of n_E/n_A is not the same as a mixing ratio, even if the units are the same, and it is classically designated by « vapor flux » when the process is integrated through time. In the case of a mixing between two air masses characterised by different water concentrations (equation 5), the addition of mixing ratios has to be weighted by the proportions of the two air masses.

- L 444: I don't understand the meaning of "until $1/q_1$ ". The composition of the additional vapor is simply given by the intercept of the linear regression, isn't it?

Presenting the two different formulations allows us to justify why we use q_E (previously q_1) instead of the intercept for determining the composition of the local vapor flux.

- L 488-498: The description of these sensitivity analyses is too vague to be understandable. Which values have been used for the humidity and isotopic composition of the third component? What is meant by "remains compatible with a linear δ_v-1/q trend"? Doesn't this depend on the choice of the input values?

We have now provided more details on the way the sensitivity analysis was performed

- L 508-510: I don't understand the meaning of this sentence.

« The d_v decrease observed when the PBL collapses corresponds to the vertical mixing of the PBL, as previously stated, and is therefore driven by the mixing with a more regional vapor.»

We have modified the sentence. In addition, we have added a second panel in Figure 7 in order to better illustrate the different phases of the daily cycles, and the associated processes.

- L 527: The global average of 10 refers to precipitation and not necessarily to water vapor. Please clarify.

In this sentence d was compared to the values observed in rainfall. Nevertheless, we have only kept the local rainfall composition (and removed the comparison with the global average), in order to simplify.

- L 534-535: "or by local evaporation" instead of "either". What is meant by "spatial significances"?

We have clarified.

1 | **Deuterium excess in atmospheric water vapour of a**
2 | **Mediterranean coastal wetland: regional versus local**
3 | **signatures**

4

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9

10

10 **Abstract**

11 Stable isotopes of water vapour represent a powerful tool for tracing atmospheric vapour
12 origin and mixing processes. Laser spectrometry recently allowed high time resolution
13 measurements, but despite an increasing number of experimental studies, there is still a need
14 for a better understanding of the isotopic signal variability at different time scales. We present
15 results of in situ measurements of $\delta^{18}\text{O}$ and δD during 36 consecutive days in summer 2011 in
16 atmospheric vapour of a Mediterranean coastal wetland exposed to high evaporation
17 (Camargue, Rhône River delta, France). The mean composition of atmospheric vapour (δ_v) is
18 $\delta^{18}\text{O}=-14.66\text{‰}$ and $\delta\text{D}=-95.4\text{‰}$, with data plotting clearly above the local meteoric water line
19 on a $\delta^{18}\text{O}$ - δD plot, and an average deuterium excess (d) of 21.9‰. Important diurnal d
20 variations are observed, and an hourly time scale analysis is necessary to interpret the main
21 processes involved in its variability. After having classified the data according to air mass
22 back trajectories, we analyse the average daily cycles relating to the two main meteorological
23 situations, i.e. air masses originating from North Atlantic and Mediterranean Sea. In both
24 situations, we show that diurnal fluctuations are driven by 1) the influence of local
25 evaporation, culminating during daytime, and leading to an increase in absolute water vapour
26 concentration associated to a δ_v enrichment and d increase; 2) vertical air mass redistribution
27 when the PBL collapses in the evening, leading to a d decrease, and 3) dew formation during
28 the night, producing a δ_v depletion with d remaining stable. Using a two-component mixing
29 model, we calculate the average composition of the locally evaporated vapour (δ_E). We find
30 higher d_E under North Atlantic air mass conditions, which is consistent with lower humidity
31 conditions. We also suggest that δ_v measured when the PBL collapses is the most
32 representative of a regional signal. Strong, cold and dry winds coming from the North bring
33 an isotopically depleted vapour, while light, warm and wet winds coming from the South
34 bring an isotopically enriched vapour. Under Northern conditions, a strong advection rate
35 dilutes the contribution of the locally evaporated vapour (δ_E) to the ambient moisture (δ_v). The
36 higher d values measured under Northern conditions, compared to the Mediterranean
37 situation, thus results from the combination of a higher d in both local and regional vapour.
38 This depiction of typical daily cycles of water vapour isotopic composition can be used as a
39 framework for further quantitative analyses of vapour sources during specific days.

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- Supprimé: At the daily time step, we show a clear separation of isotopic characteristics with respect to the air mass back trajectories, with the Northern air masses providing depleted compositions ($\delta^{18}\text{O}=-15.83\text{‰}$, $\delta\text{D}=-103.5\text{‰}$) compared to Mediterranean air masses ($\delta^{18}\text{O}=-13.13\text{‰}$, $\delta\text{D}=-86.5\text{‰}$). There is also a clear separation between d , corresponding to these different air mass origins, with higher d_v found for Northern air masses (23.2‰) than for Mediterranean air masses (18.6‰). However, since
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- Supprimé: . Based on twenty-four average hourly data, we propose a depiction of typical daily cycles of water vapor isotopic composition under the two main regional meteorological situations. D
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- Supprimé: , which indicates that regional vapor also carries a higher d_v under No(... [1]

41 1 Introduction

42 At the global scale, an acceleration of the hydrological cycle is expected in response to
43 climate change, with an intensification of both precipitation and evaporation. This effect has
44 been recognized for the ocean (Dai et al., 2009), but less conclusive patterns appear for
45 continental surfaces, especially because of the complex behaviour of land evapotranspiration
46 (Ohmura and Wild, 2002; Roderick and Farquhar, 2002; Brutsaert, 2006; Roderick et al.,
47 2007; Fu et al., 2009; Jung et al., 2010). The response of evapotranspiration to climate change
48 is controlled both by climatic and by hydrological parameters. Climate determines the
49 atmospheric evaporative demand (potential evapotranspiration), while hydrology controls
50 surface water availability, thus limiting actual evapotranspiration. In addition, continental
51 vapour is involved in land-atmosphere feedbacks such as atmospheric water recycling: high
52 evapotranspiration may contribute to regional rainfall in contexts of tropical rainforest
53 (Brubaker et al., 1993; Eltahir and Bras, 1996; van der Ent et al., 2010) or large scale
54 irrigation (Boucher et al., 2004; Tuinenburg et al., 2012), or may even reduce potential
55 evapotranspiration by lowering temperature and increasing humidities near the earth surface
56 (Destouni et al., 2010; Tuinenburg et al., 2012). A better understanding of the atmospheric
57 component of the water cycle and of the potential contribution of wetlands evaporation to the
58 regional water budget is thus important to anticipate the impact of global change, in particular
59 in Mediterranean regions where more frequent droughts are expected.

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60 Isotopic composition of atmospheric water vapour (subsequently called δ_v) represents a great
61 opportunity to explore land-atmosphere interactions, as the addition of moisture originating
62 from evapotranspiration induces a modification of the isotopic content of the background
63 vapour (Salati et al., 1979; Gat et Matsui, 1991; Gat et al., 1994; Gat, 2000; Worden et al.,
64 2007; Yamanaka and Shimizu, 2007; Vallet-Coulomb et al., 2008; Risi et al., 2013). In
65 addition, isotope tracers are now often incorporated into climate models (Sturm et al., 2005;
66 Werner et al., 2011; Risi et al., 2012, 2013) in order to improve the representation of land-
67 atmosphere interactions and feedbacks. A major challenge is thus to propose robust databases,
68 and associated methodology for data acquisition and interpretation.

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69 Laser spectrometers recently opened the door towards the high temporal resolution analysis of
70 δ_v variations, which was not possible with the traditional cold trap method. Whereas
71 cryogenic trapping provides grab samples generally averaging a couple of hours, laser

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72 spectrometry performs continuous high frequency (up to ~1 Hz) measurements of δ_v (Kerstel
73 and Gianfrani, 2008). This technology offers new insights into processes that affect the
74 isotopic composition of atmospheric water vapour and the number of studies based on
75 continuous ground level isotope measurements over multi-week periods is continuously
76 increasing, either using Tunable Diode Laser (TDL) (Lee et al., 2006; Wen et al., 2010;
77 Griffis et al., 2011; Welp et al., 2012; Wen et al., 2012), Off-Axis Integrated Cavity Output
78 Spectroscopy (OA-ICOS) (Sturm and Knohl, 2010; Sunmonu et al., 2012; Farlin et al., 2013;
79 Steen-Larsen et al., 2013) or Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-
80 CRDS) (Galewsky et al., 2011; Noone et al., 2011; Tremoy et al., 2012; Steen-Larsen et al.,
81 2013, 2014). Among these experiments are some low latitude studies which have focused on
82 the tracing of tropical or sub-tropical convective activity in West Africa (Tremoy et al., 2012)
83 or in South America (Galewsky et al., 2011). In mid latitudes (Noone et al., 2011; Farlin et
84 al., 2013), or high latitudes (Steen-Larsen et al., 2013), several studies have explored
85 atmospheric mixing processes at different time scales. Isotopes have also been used for
86 partitioning evapotranspiration into plant transpiration and direct evaporation, as the
87 associated fractionations are different (Yakir and Sternberg, 2000; Lai et al., 2006; Wang et
88 al., 2010; Griffis et al., 2011; Sun et al., 2014), for a better understanding of the role of
89 ecosystems in the hydrological cycle in the context of climate change (Wang et al., 2013).

90 However, the number of studies remains limited because of technical difficulties associated
91 with field-deployed long-term measurements. Except for some work based on cold trap
92 sampling (Jacob and Sonntag, 1991; Williams et al., 2004; Angert et al., 2008), there are to
93 our knowledge only three high time-resolution studies published from European sites
94 (Iannone et al., 2010; Kurita et al., 2012; Aemisegger et al., 2014) and none at all treating
95 Mediterranean areas. In addition, there is a need for dual tracer databases, in order to use the
96 deuterium excess signal ($d = \delta D - 8 \times \delta^{18}O$; Dansgaard, 1964) as an additional indicator of
97 atmospheric processes. Indeed, d is often considered as a indicator of evaporation conditions,
98 but its interpretation in continental vapour remains complex since it is affected by the multiple
99 vapour sources, combining the initial oceanic vapour and evapotranspiration from different
100 continental water sources (Gat et Matsui 1991; Vallet-Coulomb et al., 2008; Lai and
101 Ehleringer, 2011; Welp et al., 2012; Jouzel et al., 2013; Aemisegger et al, 2014).

102 In this paper, we provide results obtained in Camargue on 36 consecutive days during
103 summer 2011, using WS-CRDS technology. The Camargue region is emblematic of
104 Mediterranean wetlands, with important water inflow requirements and strong evaporation

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105 losses, making them highly sensitive to climate change and human pressures on water
106 resource. Our experimental site is located in the center of Camargue, close to the main lagoon
107 (Vaccarès lagoon, 65 km²). Considering the location of the site, and the important availability
108 of open water in the surroundings, we expect a dominant contribution of evaporation upon
109 transpiration fluxes. This study will provide the opportunity to investigate how local
110 evaporation combines and interact with the other regional vapour sources. We will focus on
111 identifying the main drivers of deuterium excess variability at different time scales, and
112 explore the relevance of using either relative humidity, as an indicator of evaporation
113 conditions, or specific humidity (mixing ratio) as a proxy of mixing between different vapour
114 sources. Before analysing our results, we present technical aspects of measurement calibration
115 and validation. We then analyse the day-to-day variations of δ_v and d in relation to climatic
116 parameters and the air mass back trajectories. Finally, average hourly variations are explored
117 and we interpret the typical daily cycles according to the main regional meteorological
118 conditions in order to depict their driving factors and the influence of local processes.

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120 2 Data acquisition

121 2.1 Protocols

122 Continuous in situ measurements of the isotopic composition of atmospheric water vapour
123 ($\delta^{18}\text{O}$ and δD) were performed during summer 2011 between 20 July and 24 August, at 1.75m
124 height and approximately 170m from the East border of the Vaccarès lagoon (Figure 1), using
125 Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-CRDS). The instrument we use
126 is the Picarro L1102-i isotopic liquid water and water vapour analyser (Picarro Inc.,
127 Sunnyvale, California, USA), which measures the isotopic composition of atmospheric water
128 vapour every 5 to 7 seconds. Installed in an air-conditioned room, the analyser is connected to
129 an outside air intake. As water vapour may be sticky on the walls of any tubing, a bypass
130 configuration is used to bring the air in quickly, at a rate of 6L.min⁻¹ (with a Laboport vacuum
131 pump N86 KN.18) through PVC tubing, in order to minimise wall effects that lead to
132 fractionation in the inlet. The analyser then subsamples this air at a rate lower than 0.04L.min⁻¹.
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134 Calibration of laser measurements is performed according to liquid laboratory standards, and
135 a three -way valve allows switching between the introduction of ambient air and vapour from
136 the liquid sample vaporizer (vaporization module V1102-i adjusted to 110°C for flash

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137 vaporization to avoid fractionation). We used three laboratory standards whose isotopic
138 compositions span a range of values including the composition expected in the atmosphere of
139 the Camargue (Table 1). 1.8µL of water standards is injected into the vaporizer using an
140 autosampler (CTC Analytics LEAP Technologies HTC PAL autosampler) with a SGE 5µL
141 syringe. We used synthetic air as the dry carrier gas (water content <45ppmv) delivered at a
142 pressure of 2.5±0.5psi. The analyser takes about nine minutes to perform approximately 40
143 measurements per injection, and these results are then averaged by the software. Between
144 each injection, the syringe is cleaned with 1-methyl-2-pyrrolidinone (NMP) solvent wash.
145 Our laboratory successfully participated in the IAEA 2011 proficiency test on routine analysis
146 of $\delta^{18}\text{O}$ and δD in liquid water (Wassenaar et al., 2012).

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147 Previous studies have shown that optical spectrometric methods can induce a dependence of
148 isotopic measurements on water vapour concentration (Gupta et al., 2009; Schmidt et al.,
149 2010; Johnson et al., 2011; Tremoy et al., 2011). This does not affect liquid sample
150 measurements, since the water quantity introduced into the analyser through the vaporizer is
151 nearly constant, but important variations of vapour content do occur when analysing ambient
152 atmosphere, making it necessary to correct optical measurements. We have evaluated the
153 concentration dependence of our instrument for a large range of water concentrations, and for
154 different isotopic compositions using our three standards (Figure 2). In addition, for routine
155 analyses, an evaluation of the water concentration effect is performed at approximately 24-
156 hour intervals with the more depleted standard (Standard 1) whose isotopic composition is
157 close to the atmosphere of the Camargue. The autosampler is set to perform six injections of
158 0.9µL, 1.6µL and 2.0µL in the vaporization module to obtain three water vapour
159 concentrations ranging from about 8000 to 28000ppmv, comprising values expected in the
160 study area. In addition, calibration for isotopic composition is performed at least every 24
161 hours with our three standards. For each standard, the autosampler is set to perform six
162 injections of 1.8µL in the vaporization module, corresponding to a water vapour concentration
163 of approximately 20 000ppmv. The first two injections are disregarded to remove the memory
164 effect, and the last four injections are averaged to obtain the $\delta^{18}\text{O}$ and δD measurements of
165 each standard.

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166 Gaps in time series correspond to calibration periods, but may also reflect accidental power
167 cuts or data eliminated during episodes of condensation in the tubing. This latter problem was
168 detected thanks to the use of transparent air tubing, and was easily recognizable a posteriori
169 through the abnormally smooth shape of the water vapour concentration curve. A heating

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170 cable was then used to avoid any condensation such as may occur when a negative
171 temperature gradient exists between the sampling point and the inlet of the analyser.

172

173 2.2 Dependence on water vapour concentration

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174 It has been shown that the dependence of WS-CRDS isotopic measurements on water vapour
175 concentration is specific to the individual analyser (e.g. Johnson et al., 2011; Tremoy et al.,
176 2011; Aemisegger et al., 2012). The concentration dependence of our instrument, evaluated
177 for a large range of concentrations (Figure 2), showed a linear response in the range of water
178 vapour concentration measured in the atmosphere of the Camargue (from 9000ppmv to
179 28000ppmv), with the relationship deviating slightly from the linear trend at very low and
180 high water vapour concentrations. For $\delta^{18}\text{O}$ of standards 2 and 3 there is no concentration
181 effect, but a small dependence did appear for the more depleted standard (-
182 $0.33\% \cdot 10000\text{ppmv}^{-1}$; $R^2=0.75$). For δD , we found significant regression coefficients
183 ($R^2=0.98$, 0.99 and 1.00 for standards 1, 2 and 3 respectively), and the slope of the
184 dependence was only slightly different between standards (between 7.8 and
185 $8.1\% \cdot 10000\text{ppmv}^{-1}$).

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186 This justifies the use of only one standard (Standard 1) to perform the very time-consuming
187 daily calibration of the water concentration effect (160 minutes for a 3-point calibration).
188 Measurements are corrected for concentration dependence before applying the isotopic
189 calibration in order to drive back atmospheric measurements to the water vapour
190 concentration $w_{\text{reference}}$ at which standards are measured, as follows (Schmidt et al., 2010):

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$$191 \delta_{\text{reference}} = \delta_{\text{observed}} + m \cdot (w_{\text{reference}} - w_{\text{observed}}) \quad (1)$$

192 where $\delta_{\text{reference}}$ (‰) is the reference δ value at $w_{\text{reference}}$ (20000 ppmv in our case); δ_{observed} (‰)
193 is the observed δ value at w_{observed} (ppmv) the observed concentration; m ($\% \cdot \text{ppmv}^{-1}$) is the
194 slope of the concentration dependence (Table 2).

195

196 2.3 Instrument stability

197 To evaluate the long-term stability of our instrument, statistics were calculated on raw delta
198 values measured on our three standards during the entire field measurements (Table 1).
199 Results show that the long-term variability is very low, but a regular calibration is
200 nevertheless performed. Variability of both calibrations (for water vapour concentration and

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201 isotopic composition) is shown in Table 2. For $\delta^{18}\text{O}$, the calibration for concentration appears
 202 highly variable but often flat (no concentration effect), resulting in a linearity which is not
 203 always significant ($0.26 \leq R^2 \leq 1.00$). Thus, $\delta^{18}\text{O}$ was corrected only when the concentration
 204 dependence was significant. For δD , the regression is slightly variable in the long-term, and
 205 its linearity is always significant ($0.89 \leq R^2 \leq 0.99$). For daily calibration in isotopic composition
 206 (normalisation to the VSMOW2-SLAP2 scale), we used a three-point calibration, which
 207 allows to check for the linearity of the calibration. Linear regressions between raw measured
 208 values and absolute standard compositions are established as follows for $\delta^{18}\text{O}$ and δD :

$$209 \quad \delta_{\text{calibrated}} = \text{slope} \cdot \delta_{\text{measured}} + \text{intercept} \quad (2)$$

210 Regressions are stable in the long-term (Table 2), and their linearity is always significant
 211 ($R^2=1.00$). Accuracy and precision of our instrument, estimated by considering standard 2 as a
 212 sample which has been calibrated with standards 1 and 3, show good results (Table 3). These
 213 performances are estimated on liquid measurements, and are probably lower for vapour
 214 measurements.

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216 3 Local atmospheric data

217 Hourly air temperature and relative humidity were measured at the study site. Hourly wind
 218 speed and daily PET (Potential Evapotranspiration calculated from the Penman-Monteith
 219 formula, (Monteith, 1965)) were obtained from a meteorological station located 400m far from
 220 the site of isotopic measurements. In addition, surface temperature was also measured in the
 221 main pond of the Vaccarès lagoon system at hourly time-step.

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222 Regional advection conditions were determined for each individual day by computing
 223 backward three-dimensional trajectories with the Internet-based NOAA HYSPLIT Trajectory
 224 Model (<http://ready.arl.noaa.gov/HYSPLIT.php>). The HYSPLIT (HYbrid Single-Particle
 225 Lagrangian Integrated Trajectory) model is a complete system, which allows computing
 226 simple air parcel trajectories using GDAS (Global Data Assimilation System) meteorological
 227 data. Trajectories were initialized at the station location every 24 hours at 12:00 UTC, at three
 228 heights (50, 100 and 500 meters) above ground level. A minimum back run time of 72 hours
 229 was computed, and extended, when necessary, in order to reach either the Mediterranean Sea,
 230 or the Atlantic ocean (depending of the wind regime, a maximum of 144 hours was
 231 computed). The air mass trajectories were consistent between the three different initial
 232 altitudes, and hourly data were then classified, on a daily basis (i.e. from 0:00 to 23:00).

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233 [according the three air mass origins represented in Figure 1: Mediterranean, North Atlantic, or](#)
234 [Bay of Biscay.](#)

235 Planetary boundary layer heights were obtained from GDAS meteorological data (3-hour time
236 step). They were extracted and interpolated to our specific station using the MeteoInfo
237 software (www.meteothinker.com).

238 In addition, we collected and analysed three rainfall samples corresponding to four small
239 rainfall events (25, 26, 27 July, 7 August 2011). These samples account for a total of 7.6mm
240 of the 9.6mm of cumulated rainfall during the measurement campaign; the remaining 2mm
241 correspond to eight very small events between 14 and 23 August (not sampled).

242

243 4 Results and discussion

244 The mean composition of atmospheric water [vapour](#) during the campaign is $\delta^{18}\text{O}=-14.66\text{‰}$,
245 $\delta\text{D}=-95.4\text{‰}$ and $d=21.9\text{‰}$, with significant daily variations, from $\delta^{18}\text{O}=-19.22$ to -9.96‰ and
246 $\delta\text{D}=-125.2$ to -61.7‰ , while d varies between 7.8 and 31.2‰ (Figure 3). These deuterium
247 excess values are higher than those of our three rainfall samples: 5.6‰, 4.5‰ and 7.0‰, (for
248 $\delta^{18}\text{O}=-3.89\text{‰}$, -3.7‰ , and -0.66‰ respectively), and also higher than the long-term average
249 composition of regional precipitation in the neighbouring GNIP Station (Avignon, $\approx 50\text{km}$ far
250 from the experimental site; $d = 9.2 \text{‰}$). The composition of [vapour](#) in equilibrium with
251 rainfall is plotted for comparison (Figure 3). Values slightly enriched in ^{18}O compared to
252 measured δ_v suggest a probable evaporation of rainfall in the atmosphere, a classical feature
253 [for](#) small summer rainfall events (Celle-Jeanton et al., 2001), while values slightly depleted in
254 [deuterium](#), compared to measured δ_v points to the influence of an enriched [vapour](#) at ground
255 level.

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256 In measured atmospheric vapour [composition](#), substantial day-to-day variations of δ_v are
257 observed, while d presents high hourly variations (Figure 3). In order to explore the relevant
258 time scales [to](#) interpret isotopic data in terms of synoptic and mesoscale meteorology versus
259 local influences, we first analyse the relations of our data to daily climatic variables and air
260 mass origins. Then, we focus on average diurnal variations [to](#) identify the local influences.

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262 4.1 Correlations between isotope data and local climatic parameters

263 Quite good correlations are found between daily values of δ_v and local climatic parameters
264 (Table 4), the best fit being with the mixing ratio q , ($R^2=0.72$ and 0.62 for $\delta^{18}\text{O}$ and δD

265 respectively). Such a correlation could result from the case of simple Rayleigh rainout
 266 processes, where condensation phases progressively remove water from the atmosphere and
 267 deplete the remaining atmospheric vapour in heavy isotopes (Dansgaard, 1964; Lee et al.,
 268 2006; Wen et al., 2010). The progressive rainout follows a temperature decrease, and should
 269 also result in a correlation between δ_v and T, and subsequently between rainfall isotope
 270 content (δ_p) and T, which has led to the establishment of the isotopic thermometer
 271 (Dansgaard, 1964; Jouzel et al., 1997). Our data show a relation between δ_v and T (Table 4,
 272 Figure 3) close to the isotopic thermometer: $\Delta\delta^{18}\text{O}/\Delta T=0.53\text{‰}\cdot\text{°C}^{-1}$ (Jouzel et al., 1997), but
 273 the correlation is relatively poor ($R^2=0.30$), indicating more complex processes, as was
 274 observed during a long-term German survey in which δ_v -T correlation was degraded during
 275 summer because of the admixture of vapour originating from plant transpiration (Jacob and
 276 Sonntag, 1991). Since the correlation between δ_v and q is much stronger than the δ_v -T
 277 correlation, it indicates a mixing between air masses characterized by different vapour
 278 concentrations as could result from different marine origins, and/or from the addition of
 279 continental vapour into the atmosphere.

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 281 With respect to deuterium excess, we found that q is also the best predictor of d variations at a
 282 daily time-step ($R^2=0.54$, Table 4). In addition, we observed a correlation between d and RH_a
 283 ($R^2=0.51$), consistent with Welp et al. (2012), but the correlation becomes very low ($R^2=0.19$)
 284 when using relative humidity at surface temperature (RH_s). The significance of deuterium
 285 excess in terms of a proxy for the conditions at the vapour sources comes from the fact that it
 286 is determined by the kinetic isotopic fractionation that occurs during evaporation. The kinetic
 287 fractionation mainly depends on relative humidity at the water surface, which represents the
 288 vapour concentration gradient between the liquid-vapour interface and free air (Craig and
 289 Gordon, 1965; Gonfiantini, 1986; Pfahl et Wernli, 2008; Uemura et al., 2008), Relative
 290 humidity is not conservative during air mass transport, as temperature changes modify the
 291 saturated vapour pressure, and the value measured at the meteorological station has to be
 292 reported at surface temperature.

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293 Starting from a value around d=0‰ in ocean water, the kinetic fractionation associated to the
 294 initial seawater evaporation produces an increase in d in oceanic vapour inversely related to
 295 humidity conditions (Merlivat and Jouzel, 1979; Armengaud et al., 1998; Pfahl et Wernli
 296 2008; Uemura et al 2008; Jouzel et al., 2013; Steen-Larsen et al., 2013). During the air mass
 297 trajectory over land, d may be further increased by the addition of vapour of continental origin

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298 (Gat and Matsui, 1991, Gat et al., 1994; Angert et al., 2008; Lai and Ehleringer, 2011; Welp
 299 et al., 2012). This “secondary” vapour is also expected to carry a d value inversely related to
 300 humidity conditions at the vapour source (Aemissegger et al., 2014). However, the lack of
 301 correlation between d and RH_s in our data, whilst the d-q correlation is stronger, suggests, as
 302 was the case for the δ_v -q correlation, that mixing processes between air masses characterized
 303 by different vapour origins and concentrations have weakened the d- RH_s relation.
 304 Since it is hardly modified by equilibrium condensation, d can be considered as a
 305 conservative tracer of vapour sources during mixing processes. Nevertheless, the conservative
 306 behaviour of d during rainout is perturbed by the non-linearity in the definition of deuterium
 307 excess: the delta-notation approximation induces a small shift in d when there is a large
 308 decrease in $\delta^{18}O$ and δD (Gat et al., 1996; Angert et al., 2008; Welp et al., 2012). In the
 309 observed range of $\delta^{18}O$ (from -11 to -18‰), we have estimated this effect to induce a 2.5‰
 310 increase in d, while the substantial variations in d observed in our daily data are significantly
 311 higher (from 15 to 26‰), allowing the use of d as a tracer of different vapour pools.

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313 4.2 Regional isotopic signatures

314 In order to examine the link between the isotopic characteristics of vapour and the air mass
 315 origin, we analyse the data classified according to the three main backward trajectories
 316 schematically represented in Fig. 1 (see section 3). Corresponding hourly data are scattered in
 317 the $\delta^{18}O$ - δD plot distinctly above the local meteoric water line (LMWL, Figure 4), and show
 318 isotopically depleted compositions for air masses coming from the North Atlantic, while air
 319 masses coming from the Mediterranean Sea display isotopically enriched vapour (Table 5,
 320 Figure 4). For air masses coming from Bay of Biscay, hourly data encompass the entire
 321 isotopic range. Local climatic data associated with the three meteorological situations reflect
 322 synoptic weather conditions related to air mass origins. Air masses coming from the North
 323 Atlantic are associated with strong, cold, and dry winds, while those from the Mediterranean
 324 are associated on the contrary with light, warm and wet winds (Table 5). The Bay of Biscay is
 325 an intermediate situation. It thus appears that the greater the distance over land (Figure 1), the
 326 more depleted δ_v . The northern trajectory corresponds to a “Mistral” situation: a typical strong
 327 north-northwest wind that affects the north of the occidental Mediterranean basin 130 days a
 328 year on average. The air mass is gradually dried out by rainout processes over land and
 329 accelerated in the Rhône River Valley and acquires a depleted isotopic signature. On the

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330 contrary, an air mass travelling over the Mediterranean Sea with the slight thermal wind or
331 sea breeze coming from the South is moistened and acquires and maintains an enriched
332 isotopic signature.

333 With respect to δD , North Atlantic air masses bring higher values (23.2‰) than Mediterranean
334 air masses (18.6‰), but the main feature, which appears on the $\delta^{18}O$ - δD plot (Figure 4), is the
335 distinct separation between nocturnal and diurnal hourly data, with the latter plotting higher
336 above the meteoric lines. This feature is observed for each of the three air mass origins.

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337 Within these three classes of data, strong linear relationships are observed (Figure 4), with
338 slopes lower than eight, a value attributed to thermodynamic equilibrium, as it approximately
339 represents the average ratio between D and ^{18}O liquid-vapour equilibrium fractionation. Such
340 low slopes have also been observed in atmospheric vapour from Hawaii (7.02 (Bailey et al.,
341 2013)), Greenland (between 6.47 and 7.44 (Steen-Larsen et al., 2013)), Western Siberia
342 (between 5.6 and 7.7 (Bastrikov et al., 2014)), and in North America (7.5 (Berkelhammer et
343 al., 2013)). The previously described shift in δD during Rayleigh-type rainout, due to the non-
344 linearity in the deuterium excess definition, is not sufficient to explain these low slopes, and
345 non-equilibrium processes such as evaporation are also probably involved (Gibson et al.,
346 2008).

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348 4.3 Analysis of average daily cycles

349 In order to observe the diurnal variations suggested by the night-day separation, average daily
350 cycles of isotopic and climatic data are plotted for the three air mass origins (Figure 5). A
351 well-pronounced cyclicity appears for δD in each meteorological condition. For the Bay of
352 Biscay origin, the average δD cycle is very similar to the North Atlantic case, with larger
353 standard deviations, reflecting a more variable climatic situation. For Mediterranean
354 conditions, the δD cycle is higher in amplitude than for North Atlantic conditions, and lower in
355 absolute values, especially during the night. The high standard deviations observed during the
356 last hours of the day correspond to calibration periods for which there are fewer data, but may
357 also be due to variations in the timing of the PBL evening transition. The increase in δD during
358 the morning is mainly associated with a δD increase, while $\delta^{18}O$ variations are smoother.
359 Amplitudes of daily isotopic variations are higher for Mediterranean conditions (9.7‰,
360 16.2‰ and 1.3 ‰ for δD , $\delta^{18}O$ and $\delta^{18}O$ respectively) than for North Atlantic ones (7.0‰,
361 13.1‰ and 1.1‰ for δD , $\delta^{18}O$ and $\delta^{18}O$ respectively).

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362 From a climatic point of view, we observe high diurnal variations in RH_a , mainly driven by
363 the large amplitude of air temperature variations between night and day (Figure 5). As
364 discussed above, the significance of relative humidity conditions in terms of evaporation
365 conditions – and deuterium excess control – is only relevant at surface temperature. The
366 variations are smoother for RH_s , and it more or less follows the absolute amount of water
367 (Figure 5). Under Mediterranean conditions, a distinct increase of q occurs in the morning,
368 indicating a net addition of vapour in the atmosphere. Under North Atlantic conditions, the q
369 increase is lower, but still detectable.

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370 The daily cyclicality of the planetary boundary layer height (PBLH) is specifically related to the
371 different atmospheric conditions. The PBLH attains around 1100m on average during the
372 afternoon under North Atlantic and Bay of Biscay conditions, with a significant standard
373 deviation. Under Mediterranean conditions, the PBLH is less variable and remains at almost
374 700m. Nocturnal values are also very low -less than 100m- in Mediterranean conditions,
375 compared to 400-500m in the other weather situations (Figure 5). Low PBLH in
376 Mediterranean conditions corresponds to weak turbulence and air stability resulting from light
377 winds, while Northerly advection transports a relatively cold air mass over a warmer surface,
378 leading to a weaker stratification.

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380 Daytime processes: contribution of local evaporation

381 The diurnal increase in d is a widely observed feature, which reflects the diurnal variation of
382 the water and air mass balances of the planetary boundary layer (Lai and Ehleringer, 2011).
383 This increase can be caused by the entrainment of free atmosphere into the boundary layer
384 (Zhang et al., 2011; Welp et al., 2012; Berkelhammer et al., 2013), but also by the addition of
385 locally evaporated vapour. The direction of vapour concentration changes associated with
386 these d variations can help to identify which of these two processes dominates the PBL water
387 mass budget. Entrainment brings a dryer air into the PBL, and thus causes a daytime decrease
388 in vapour concentration, while an increase in mixing ratio indicates the addition of an
389 evaporation flux. Note that the transpiration component of evapotranspiration is not expected
390 to carry high d , as it has the same isotopic composition as the soil water at steady state (Yakir
391 and Wang, 1996; Williams et al., 2004). In addition, the free atmospheric air is characterized
392 by a isotopically lighter vapour (He and Smith, 1999; Bailey et al., 2013; Berkelhammer, et al
393 2013), and the dominance of entrainment during daytime is generally associated with a δ_v

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394 depletion (Lai et al., 2006; Lai and Ehleringer, 2011; Tremoy et al., 2012; Bailey et al., 2013;
 395 Berkelhammer, et al 2013). Welp et al. (2012) compared six measurement locations and
 396 found that both local evapotranspiration and entrainment were involved: in some of their sites,
 397 the d daily increase was associated with a $\delta^{18}\text{O}$ decrease during the early morning due to
 398 entrainment of free atmosphere into the boundary layer during convective mixing, while the
 399 subsequent slight $\delta^{18}\text{O}$ increase came from evapotranspiration. Our data display a
 400 simultaneous increase in q , $\delta^{18}\text{O}$ and δD (Figure 5), and thus indicates that the addition of
 401 surface vapour is the dominant process governing the d cyclicity during the day.

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403 Nocturnal processes: dew formation

404 In each meteorological situation, d displays an abrupt decrease at around 20:00 UTC, which
 405 corresponds to the timing of sunset. Afterwards, during the 20:00-6:00 UTC period, d remains
 406 low, while δ_v follows a gradual depletion associated with a q decrease (Figure 5). This
 407 corresponds to the effect of a progressive Rayleigh-condensation process, and indicates the
 408 formation of dew induced by the nocturnal cooling of soil and/or leaves surfaces, as was
 409 observed by Berkelhammer et al. (2013).

410 A small nocturnal evaporation of the lagoon water could nevertheless occur since the water
 411 surface temperature remains high and maintains RH_s below saturation (Figure 5), but it is
 412 expected to remain low compared to daytime fluxes. During the night, the PBL subsidence
 413 corresponds to the reduction of both the surface heat fluxes and entrainment, and the addition
 414 of water vapour to the atmosphere, if any, remains low. The large-scale motion becomes
 415 dominant and, without changing the total PBL mass, redistributes it horizontally (Medeiros et
 416 al., 2005). The nocturnal isotopic values thus represent the average composition of the PBL,
 417 onto which are superimposed daytime fluxes. More precisely, since dew formation is a local
 418 process, the value measured just after the sunset (20:00 UTC), when the PBL collapses, is
 419 probably the most representative composition of the average PBL, with the greater proportion
 420 of regional water vapour. The high d values observed during the night (on average 15,1
 421 $\pm 0,5\text{‰}$ under Mediterranean conditions and 20.9 $\pm 0,7\text{‰}$ under North Atlantic conditions),
 422 thus result from the remaining imprint of local evaporation, combined with the signature of
 423 the regional atmosphere.

424

4.4 Local isotopic signatures

The concomitant increase of q and d during daytime in our average diurnal cycles indicates that the d cyclicity is mainly driven by the addition of surface vapour fluxes. As stated above, the location of the experimental site close to the main lagoon, and the availability of large open water areas in the surroundings, point to a dominant contribution of evaporation over transpiration. In order to calculate the isotopic composition of the locally evaporated vapour (δ_E), we use a two-component mixing model based on the linear correlation between $1/q$ and δ_v , derived from the “Keeling plot” method. The ability of this simple model to describe our data and the possible contribution of regional advection is then discussed. The original Keeling approach (Keeling, 1958) was initially proposed to describe the addition of CO_2 into the atmosphere, and then further used to determine the isotopic composition of evapotranspired vapour flux (Yakir and Sternberg, 2000; Yepez et al., 2003; Williams et al., 2004; Wang et al., 2010; Zhang et al., 2010; Noone et al., 2011; Lee et al., 2012; Griffis et al., 2013; Noone et al., 2013). Assuming a background represented by an initial air quantity with a mixing ratio q_{BG} (mmol/mol), and taking n_A (mol) the corresponding dry air amount, the addition of water vapour n_E (mmol) leads to the following mixing equation:

$$q = q_{BG} + \frac{n_E}{n_A} \quad (3)$$

where q is the mixing ratio (mmol/mol) of the resulting humid air (note that n_E/n_A does not represent a mixing ratio despite same units). Attributing an isotopic composition to each of these vapour pools, δ_{BG} for the background vapour and δ_E for the added vapour, the corresponding isotopic mass balance is:

$$\delta_v = (\delta_{BG} - \delta_E) \cdot \frac{q_{BG}}{q} + \delta_E \quad (4)$$

where δ_v is the vapour composition of the resulting atmosphere. In a data set tracing the progressive addition of pure vapour in a closed system, and assuming an isotopically stable background, the δ_v versus $1/q$ relationship displays a linear trend. The composition of the added vapour δ_E is therefore deduced from the intercept (for $q \rightarrow \infty$).

However, when the increase in water vapour concentration results from the mixing with a humid air mass, equation (3) becomes:

$$q = xq_{BG} + (1-x)q_E \quad (5)$$

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454 Where x is the fraction of the initial background air, and q_E is the mixing ratio of the added air
 455 mass (mmol/mol). Thus, the corresponding expression for δ_v is:

$$456 \quad \delta_v = (\delta_{BG} - \delta_E) \cdot \frac{xq_{BG}}{q} + \delta_E \quad (6)$$

457 The composition of the added vapour is then deduced from the δ_v versus $1/q$ plot for $x=0$, i.e.
 458 for $q=q_E$ and the mixing ratio of the added air (q_E) is a prerequisite for applying this two-
 459 component mixing model. For a humid air mass coming from open water evaporation, a
 460 mixing ratio corresponding to saturation conditions at the liquid-vapour interface ($q_E = q_s$)
 461 can be considered as representing the limit condition (Craig and Gordon, 1965; Noone et al.,
 462 2011; Noone, 2012).

463 Our discussion will focus on the two most contrasted meteorological situations, i.e.
 464 Mediterranean and North Atlantic air mass origins. Strong correlations are found between
 465 average values of δ_v and $1/q$ for the period of q increase, i.e. 05:00-13:00 UTC for North
 466 Atlantic situations and 05:00-10:00 UTC for Mediterranean situations (R^2 values are between
 467 0.85 and 0.96, see Figure 6). The local end-members are calculated for the average value of
 468 saturation mixing ratio at the water surface temperature (q_s), during the daily maximum air
 469 water concentrations (at 13:00 UTC or 10:00 UTC). Uncertainties are determined as resulting
 470 from error propagation of the linear model in the whole range of q_s standard deviation. The
 471 resulting compositions of local end-members (δ_E) are: $\delta^{18}O = -12.5\%$ (-11.0‰ to -13.9‰);
 472 $\delta D = -48\%$ (-30‰ to -64‰) for North Atlantic conditions, $\delta^{18}O = -11.8\%$ (-11.0‰ to -12.5‰);
 473 $\delta D = -58\%$ (-46‰ to -68‰) for Mediterranean conditions (Figure 7). High deuterium excess
 474 values characterize the surface vapour for North Atlantic ($d = 52 \pm 29\%$) and Mediterranean
 475 conditions ($37 \pm 17\%$), which is consistent with previous estimates from the Craig and
 476 Gordon model (Craig and Gordon, 1965; Gat et al, 1994). Such high d is a characteristic of
 477 vapour coming from continental evaporation and allowed to detect the contribution of
 478 continental vapour to regional precipitation (Gat et Matsui, 1991; Gat et al, 1994; Vallet-
 479 Coulomb et al., 2008). In our case, these high d values confirm that evaporation is largely
 480 dominant over transpiration, and that the higher d under North Atlantic air mass conditions is
 481 consistent with lower RH_s , compared to Mediterranean conditions (Figure 5, Table 5).

482 Going on with the two end-member mixing assumption, this δ_E composition could be used to
 483 interpret the amplitude of diurnal δ_v variations in terms of the daily addition of locally
 484 evaporated vapour to the nocturnal background. The lower amplitude of diurnal variations

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 The ...ation of... thus requires the knowledge of the vapor content of the added air... If it es... we can use the... which ...
 Indeed, as described by the diffusion model of Craig & Gordon (1965), evaporation results from the diffusion of vapor between a saturation concentration at the water-air interface and open air. ... [4]

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 from a simple isotopic mass balance...

$$\frac{n_E}{n_v} = \frac{\delta_v - \delta_{BG}}{\delta_E - \delta_{BG}} \quad (7)$$
 Where W_E/W represents the mass (or molar) ratio of local vapor to total atmospheric moisture, $\delta_{v(\min)}$ corresponds to the vapor background and $\delta_{v(\max)}$ is the maximum contribution of local vapor. We find 21% of local vapor in the ambient moisture under North Atlantic conditions, consistently when using $\delta^{18}O$ and δD compositions, and 43 to 48% under Mediterranean conditions, when using δD and $\delta^{18}O$ mass balances, respectively. ... [6]

485 observed under North Atlantic condition (Figure 7) would then indicate a lower proportion of
 486 locally evaporated vapour in ambient moisture. However, this is not consistent with the
 487 stronger average potential evapotranspiration rates under North Atlantic conditions, compared
 488 to the Mediterranean situation: $5.8\text{mm}\cdot\text{day}^{-1}$ versus $3.8\text{mm}\cdot\text{day}^{-1}$ (Table 5). This apparent
 489 contradiction indicates that the isotopic imprint of local evaporation is diluted by advection,
 490 with a greater extend under Northern conditions than under Mediterranean conditions. This is
 491 fully consistent with the high wind speed characterizing North Atlantic conditions: an average
 492 value of $2.0\text{ m}\cdot\text{s}^{-1}$ compared to $0.7\text{ m}\cdot\text{s}^{-1}$ for Mediterranean conditions. Local vapour is thus
 493 flushed by advection of dry northward air masses, and since this advected vapour may carry a
 494 different isotopic signature than the nocturnal background, a simple two-component mixing
 495 model is not sufficient to describe the PBL water balance.

496 We have evaluated the impact of regional advection on the determination of δ_E , by testing
 497 different simulations of a 3-component mixing process. Starting from the initial background
 498 (δ_{BG} = average δ_v value at 5:00 UTC), we simulate the progressive addition of both regional
 499 advected vapour (δ_R) and locally evaporated vapour (δ_E), and we compare the resulting
 500 composition with observed δ_v during the q-increase period of the day. For each simulation, we
 501 choose an hypothetical value of δ_R , and we adjust δ_E in order to match the observed data on
 502 the δ_v versus $1/q$ relationship, using a simple trial-and-error procedure, successively for $\delta^{18}\text{O}$
 503 and δD . We have tested a range of δ_R values compatible with the shift observed during sunset,
 504 on the $\delta^{18}\text{O}$ - δD plot (Figure 7). As discussed previously, the δ_v value measured at 20:00 UTC
 505 is expected to carry the lowest proportion of locally evaporated vapour. We thus postulate that
 506 the shift in d observed at 20:00 (“B” arrow in Figure 7) is “dragged” by the composition of a
 507 more regional vapour. We have then explored a domain of δ_R values limited by: 1) the 20:00
 508 UTC value as an upper limit for δD ; 2) the 20:00 UTC (05:00 UTC) value as a lower limit for
 509 $\delta^{18}\text{O}$ under Mediterranean (North Atlantic) conditions and 3) the LMWL. For each δ_R value,
 510 different mixing ratio were tested (q_R), chosen to remain compatible with the midday-20:00
 511 UTC trend observed on the $1/q$ - δ_v plot. We found that in all cases, the δ_E values remain in the
 512 range of the error bars shown in Figure 7, with slightly lower $\delta^{18}\text{O}$ and higher d.

513 The processes involved in the diurnal isotopic behaviour of atmospheric vapour can be
 514 summarized in the $\delta^{18}\text{O}$ - δD plot, which is a good mean to understand the drivers of d
 515 variations (Figure 7). The two clusters of average vapour data are distributed along two linear
 516 trends defined by the q-increase period of the day (“A” arrow in Figure 7), which also meet

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517 the calculated value of δ_E . These trends result from the addition of locally evaporated vapour
 518 into the ambient air, but, as discussed above, are also influenced by the input of (and flushing
 519 by) regional advection. The daytime vapour composition then oscillates, but stays around the
 520 maximum δ_v value, until the abrupt shift that occurs at 20:00 UTC, during sunset, consistently
 521 for both meteorological situations (“B” arrow in Figure 7). The d decrease observed when the
 522 PBL collapses, during sunset, corresponds to the weakening of surface evaporation, and to an
 523 increasing proportion of a more regional atmosphere. The night-time δ_v evolves closer to the
 524 meteoric water line, compared to daytime compositions. The progressive condensation
 525 occurring between 20:00 and 05:00 UTC maintains the δ_v along a regression line roughly
 526 parallel to the LMWL (“C” arrow in Figure 7).

527 The stronger advection rate which prevails under North Atlantic conditions, and which
 528 smoothed the diurnal amplitude of δ_v variation, suggests that the higher d signature of water
 529 vapour (Table 5) results from the combined influences of higher d in the locally evaporated
 530 vapour and in the regional vapour, consistently with the longer continental trajectory. A more
 531 precise determination of the regional vapour isotopic composition would rely on the
 532 quantification of advection fluxes and on a full PBL mass balance estimate.

534 5 Conclusion

535 Our results show that both local and regional isotopic signatures are recorded in the ground
 536 level atmospheric vapour composition, and that a sub-daily analysis is necessary to decipher
 537 these influences. After having classified the data according to air mass origins and
 538 trajectories, we found strong diurnal variations of d , with lower amplitude variations under
 539 the influence of Northern air masses than under Mediterranean influences. The higher average
 540 d observed under Northern conditions (23.2‰ compared to 18.6‰ for the Mediterranean
 541 situations) is mainly due to higher nocturnal values, while the daytime maxima are similar.
 542 However, the drivers of these diurnal variations have to be understood to interpret the isotopic
 543 signal with respect to its relevant spatiotemporal scales, and it is essential to understand and
 544 compare the behaviour of both $\delta^{18}\text{O}$ and δD (referred to as δ_v) to understand d .

545 A diurnal increase in d can be caused by entrainment of free atmospheric air, by surface
 546 evaporation, or by a combination of both processes. Unlike evaporation, the contribution of
 547 free atmospheric air would induce a decrease in absolute vapour concentration. Therefore, our
 548 average daily cycles clearly indicate that the diurnal increase in d is essentially driven by local

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549 evaporation. Based on the robust alignment of average hourly data in a δ_v versus $1/q$ plot for
550 the q-increase period of the day, we applied a two-component mixing model to estimate the
551 composition of locally evaporated vapour (δ_E). Then, since regional advection modulates the
552 amplitude of diurnal δ_v variations, we discussed the two-component mixing assumption and
553 evaluate the influence of a third component on the determination of δ_E . We show that it
554 remains low, because the composition of regional advection is expected to be close to the
555 nocturnal values. We found higher d for the locally evaporated vapour under North Atlantic
556 air mass conditions, which is consistent with lower humidity conditions, while the
557 corresponding $\delta^{18}O$ compositions are very similar between the two meteorological situations,
558 with a difference of about 0.7‰.

559 In contrast, there is an important difference in the $\delta^{18}O$ compositions between the two
560 meteorological situations when considering the nocturnal values. More specifically, it is
561 interesting to consider the ambient vapour composition measured at 20:00 UTC when the
562 PBL collapses, and before the progressive influence of dew formation during the night. This
563 20:00 UTC composition is the least influenced by locally evaporated vapour, and the most
564 representative of a regional signal. The difference in $\delta^{18}O$ between the two main
565 meteorological situations (upper than 3‰) reflects the influence of synoptic and mesoscale
566 weather conditions, related to air mass origin and trajectory. Strong, cold and dry winds
567 coming from the North bring an isotopically depleted vapour. Conversely, light, warm and
568 wet winds coming from the South bring an isotopically enriched vapour. In addition, the
569 strong advection rate that prevails under North-Atlantic conditions suggests that, in this
570 situation, the high average d of water vapour at 20:00 UTC also reflects the signature of
571 regional vapour.

572 In general, our data showed that the mixing ratio is a better predictor of deuterium excess
573 variations than relative humidity, at both daily and sub-daily time scales, since mixing
574 processes between different vapour sources weakened the relevance of relative humidity as an
575 indicator of evaporation conditions. At the daily time step, the mixing ratio is a proxy for the
576 air mass origin, since there is a huge contrast between water content of Northern and
577 Mediterranean air masses. At the sub-daily time step, a δ_v -q correlation, and subsequently a d-
578 q correlation, during the q-increase period of the day, results from the addition of locally
579 evaporated vapour. The general framework proposed in this study, for typical daily cycles of

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580 water vapour isotopic composition under different meteorological conditions, could be used in
581 further quantitative analyses of vapour sources during specific days.

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592 **References**

- 593 [Aemisegger, F., Sturm, P., Graf, P., Sodemann, H., Pfahl, S., Knohl, A., and Wernli, H.:](#)
594 [Measuring variations of \$\delta^{18}\text{O}\$ and \$\delta^2\text{H}\$ in atmospheric water vapour using two commercial](#)
595 [laser-based spectrometers: an instrument characterisation study, *Atmos. Meas. Tech.*, 5, 1491-](#)
596 [1511, doi:10.5194/amt-5-1491-2012, 2012.](#)
- 597 Aemisegger, F., Pfahl, S., Sodemann, H., Lehner, I., Seneviratne, S. I. and Wernli, H.:
598 Deuterium excess as a proxy for continental moisture recycling and plant transpiration,
599 *Atmos. Chem. Phys.*, 14, 4029–4054, doi:10.5194/acp-14-4029-2014, 2014.
- 600 Angert, A., Lee, J.-E. and Yakir, D.: Seasonal variations in the isotopic composition of near-
601 surface water vapour in the eastern Mediterranean, *Tellus B*, 60, 674–684,
602 doi:10.1111/j.1600-0889.2008.00357.x, 2008.
- 603 Armengaud, A., Koster, R. D., Jouzel, J. and Ciais, P.: Deuterium excess in Greenland snow:
604 Analysis with simple and complex models, *J. Geophys. Res.*, 103, 8947–8953, 1998.
- 605 Bailey, A., Toohey, D. and Noone, D.: Characterizing moisture exchange between the
606 Hawaiian convective boundary layer and free troposphere using stable isotopes in water, *J.*
607 *Geophys. Res. Atmos.*, 118, 8208–8221, doi:10.1002/jgrd.50639, 2013.
- 608 Bastrikov, V., Steen-Larsen, H. C., Masson-Delmotte, V., Griбанov, K., Cattani, O., Jouzel, J.
609 and Zakharov, V.: Continuous measurements of atmospheric water vapour isotopes in western
610 Siberia (Kourovka), *Atmos. Meas. Tech.*, 7, 1763–1776, doi:10.5194/amt-7-1763-2014, 2014.
- 611 Berkelhammer, M., Hu, J., Bailey, A., Noone, D. C., Still, C. J., Barnard, H., Gochis, D.,
612 Hsiao, G. S., Rahn, T. and Turnipseed, A.: The nocturnal water cycle in an open-canopy
613 forest, *J. Geophys. Res. Atmos.*, 118, 10,225–10,242, doi:10.1002/jgrd.50701, 2013.
- 614 Boucher, O., Myhre, G. and Myhre, A.: Direct human influence of irrigation on atmospheric
615 water vapour and climate, *Clim. Dyn.*, 22, 597–603, doi:10.1007/s00382-004-0402-4, 2004.
- 616 Brubaker, K. L., Entekhabi, D. and Eagleson, P. S.: Estimation of Continental Precipitation
617 Recycling, *J. Clim.*, 6, 1077–1089, 1993.
- 618 Brutsaert, W.: Indications of increasing land surface evaporation during the second half of the
619 20th century, *Geophys. Res. Lett.*, 33, L20403, doi:10.1029/2006GL027532, 2006.
- 620 Celle, H., Daniel, M., Mudry, J. and Blavoux, B.: Signal pluie et traçage par les isotopes
621 stables en Méditerranée occidentale. Exemple de la région avignonnaise (Sud-Est de la
622 France), *C. R. Acad. Sci. Paris, Earth Planet. Sci.*, 331, 647–650, 2000.
- 623 Celle-Jeanton, H., Travi, Y. and Blavoux, B.: Isotopic typology of the precipitation in the
624 Western Mediterranean region at three different time scales, *Geophys. Res. Lett.*, 28, 1215–
625 1218, 2001.

- 626 Craig, H. and Gordon, L. I.: Deuterium and oxygen 18 variations in the ocean and the marine
627 atmosphere, in *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, edited by E.
628 Tongiorgi, pp. 9–130, Spoleto, Italy., 1965.
- 629 Dai, A., Qian, T., Trenberth, K. E. and Milliman, J. D.: Changes in Continental Freshwater
630 Discharge from 1948 to 2004, *J. Clim.*, 22, 2773–2792, doi:10.1175/2008JCLI2592.1, 2009.
- 631 Dansgaard, W.: Stable isotopes in precipitation, *Tellus*, 16, 436–468, 1964.
- 632 Destouni, G., Asokan, S. M. and Jarsjö, J.: Inland hydro-climatic interaction: Effects of
633 human water use on regional climate, *Geophys. Res. Lett.*, 37, L184402,
634 doi:10.1029/2010GL044153, 2010.
- 635 | Eltahir, E. A. B. and Bras, R. L.: [Precipitation recycling](#), *Rev. Geophys.*, 34, 367–378, 1996.
- 636 Farlin, J., Lai, C.-T. and Yoshimura, K.: Influence of synoptic weather events on the isotopic
637 composition of atmospheric moisture in a coastal city of the western United States, *Water*
638 *Resour. Res.*, 49, 3685–3696, doi:10.1002/wrcr.20305, 2013.
- 639 Fu, G., Charles, S. P. and Yu, J.: A critical overview of pan evaporation trends over the last
640 50 years, *Clim. Change*, 97, 193–214, doi:10.1007/s10584-009-9579-1, 2009.
- 641 Galewsky, J., Rella, C., Sharp, Z., Samuels, K. and Ward, D.: Surface measurements of upper
642 tropospheric water vapor isotopic composition on the Chajnantor Plateau, Chile, *Geophys.*
643 *Res. Lett.*, 38, L17803, doi:10.1029/2011GL048557, 2011.
- 644 | [Gat, J. R.: Oxygen and hydrogen isotopes in the hydrologic cycle. *Annu. Rev. Earth Planet.*](#)
645 [*Sci.* 24, 225-262, 1996.](#)
- 646 Gat, J. R.: Atmospheric water balance — the isotopic perspective, *Hydrol. Process.*, 14,
647 1357–1369, 2000.
- 648 Gat, J.R., Matsui, E.: Atmospheric water balance in the Amazon basin: an isotopic
649 evapotranspiration model. *J. Geophys. Res.*, 96, D7, 13179-13188, 1991.
- 650 Gat, J.R., Bowser, C.J., Kendall, C.: The contribution of evaporation from the Great Lakes to
651 the continental atmosphere: estimate based on stable isotope data. *Geophys. Res. Lett.*, 21, 7,
652 557-560, 1994.
- 653 Gat, J. R., Shemesh, A., Tziperman, E., Hecht, A., Georgopoulos, D. and Basturk, O.: The
654 stable isotope composition of waters of the eastern Mediterranean Sea, *J. Geophys. Res.*, 101,
655 6441–6451, 1996.
- 656 Gibson, J. J., Birks, S. J., and Edwards, T. W. D. : Global prediction of δA and $\delta 2H$ - $\delta 18O$
657 evaporation slopes for lakes and soil water accounting for seasonality, *Tellus*, 16, 436-468,
658 doi:10.1111/j.2153- 3490.1964.tb00181.x, 2008.
- 659

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- 660 Gonfiantini, R.: Environmental isotopes in lake studies, in: Handbook of Environmental
661 Isotope geochemistry, 2, Fritz, P. and Fontes, J. C. Editors., Elsevier, Amsterdam, 113-163,
662 1986.
- 663 Griffis, T. J.: Tracing the flow of carbon dioxide and water vapor between the biosphere and
664 atmosphere: A review of optical isotope techniques and their application, Agric. For.
665 Meteorol., 174-175, 85–109, doi:10.1016/j.agrformet.2013.02.009, 2013.
- 666 Griffis, T. J., Lee, X., Baker, J. M., Billmark, K., Schultz, N., Erickson, M., Zhang, X.,
667 Fassbinder, J., Xiao, W. and Hu, N.: Oxygen isotope composition of evapotranspiration and
668 its relation to C4 photosynthetic discrimination, J. Geophys. Res., 116, G01035,
669 doi:10.1029/2010JG001514, 2011.
- 670 Gupta, P., Noone, D., Galewsky, J., Sweeney, C. and Vaughn, B. H.: Demonstration of high-
671 precision continuous measurements of water vapor isotopologues in laboratory and remote
672 field deployments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS)
673 technology, Rapid Commun. Mass Spectrom., 23, 2534–2542, doi:10.1002/rcm.4100, 2009.
- 674 He, H. and Smith, R. B.: Stable isotope composition of water vapor in the atmospheric
675 boundary layer above the forests of New England, J. Geophys. Res., 104, 11,657–11,673,
676 1999.
- 677 IAEA: Reference Sheet for VSMOW2 and SLAP2 international measurement standards.
678 Issued 2009-02-13, International Atomic Energy Agency, Vienna , 5 p.,
679 http://curem.iaea.org/catalogue/SI/pdf/VSMOW2_SLAP2.pdf, 2009.
- 680 [Iannone, R. Q., D. Romanini, O. Cattani, H. A. J. Meijer, and E. R. Th. Kerstel: Water](#)
681 [isotope ratio \(d2H and d18O\) measurements in atmospheric moisture using an optical](#)
682 [feedback cavity enhanced absorption laser spectrometer, J. Geophys. Res., 115, D10111,](#)
683 [doi:10.1029/2009JD012895, 2010.](#)
- 684 Jacob, H. and Sonntag, C.: An 8-year record of the seasonal variation of 2H and 18O in
685 atmospheric water vapour and precipitation at Heidelberg, Germany, Tellus B, 43, 291–300,
686 1991.
- 687 Johnson, L. R., Sharp, Z. D., Galewsky, J., Strong, M., Van Pelt, A. D., Dong, F. and Noone,
688 D.: Hydrogen isotope correction for laser instrument measurement bias at low water vapor
689 concentration using conventional isotope analyses: application to measurements from Mauna
690 Loa Observatory, Hawaii., Rapid Commun. mass Spectrom., 25, 608–616,
691 doi:10.1002/rcm.4894, 2011.
- 692 Jouzel, J., Alley, R. B., Cuffey, K. M., Dansgaard, W., Grootes, P., Hoffmann, G., Johnsen, S.
693 J., Koster, R. D., Peel, D., Shuman, C. A., Stievenard, M., Stuiver, M. and White, J.: Validity
694 of the temperature reconstruction from water isotopes in ice cores, J. Geophys. Res., 102,
695 26,471–26,487, 1997.
- 696 Jouzel, J., Delaygue, G., Landais, A., Masson-Delmotte, V., Risi, C. and Vimeux, F.: Water
697 isotopes as tools to document oceanic sources of precipitation, Water Resour. Res., 49, 7469–
698 7486, doi:10.1002/2013WR013508, 2013.

699 Jung, M., Reichstein, M., Ciais, P., Seneviratne, S. I., Sheffield, J., Goulden, M. L., Bonan,
700 G., Cescatti, A., Chen, J., de Jeu, R., Dolman, A. J., Eugster, W., Gerten, D., Gianelle, D.,
701 Gobron, N., Heinke, J., Kimball, J., Law, B. E., Montagnani, L., Mu, Q., Mueller, B., Oleson,
702 K., Papale, D., Richardson, A. D., Rouspard, O., Running, S., Tomelleri, E., Viovy, N.,
703 Weber, U., Williams, C., Wood, E., Zaehle, S. and Zhang, K.: Recent decline in the global
704 land evapotranspiration trend due to limited moisture supply, *Nature*, 467, 951–954,
705 doi:10.1038/nature09396, 2010.

706 | Keeling, C. D.: The concentration and isotopic abundances of atmospheric carbon dioxide in
707 rural areas, *Geochim. Cosmochim. Acta*, 13, 322–334, 1958.

708 | [Kerstel, E. and Gianfrani, L.: Advances in laser-based isotope ratio measurements: selected
709 applications, *Appl. Phys. B-Lasers O.*, 92, 439-449, 2008.](#)

710 Kurita, N., Newman, B. D., Araguas-Araguas, L. J., Aggarwal, P.: Evaluation of continuous
711 water vapor δD and $\delta^{18}O$ measurements by off-axis integrated cavity output spectroscopy,
712 *Atmos. Meas. Tech.*, 5, 2069-2080, 2012.

713 Lai, C.-T., Ehleringer, J. R., Bond, B. J. and Paw U, K. T.: Contributions of evaporation,
714 isotopic non-steady state transpiration and atmospheric mixing on the $\delta^{18}O$ of water vapour
715 in Pacific Northwest coniferous forests, *Plant, Cell Environ.*, 29, 77–94, 2006.

716 Lai, C.-T. and Ehleringer, J. R.: Deuterium excess reveals diurnal sources of water vapor in
717 forest air., *Oecologia*, 165, 213–223, doi:10.1007/s00442-010-1721-2, 2011.

718 Lee, X., Smith, R. and Williams, J.: Water vapour $^{18}O/^{16}O$ isotope ratio in surface air in
719 New England, USA, *Tellus B*, 58, 293–304, doi:10.1111/j.1600-0889.2006.00191.x, 2006.

720 Lee, X., Huang, J. and Patton, E. G.: A Large-Eddy Simulation Study of Water Vapour and
721 Carbon Dioxide Isotopes in the Atmospheric Boundary Layer, *Boundary-Layer Meteorol.*,
722 145, 229–248, doi:10.1007/s10546-011-9631-3, 2012.

723 Medeiros, B., Hall, A. and Stevens, B.: What Controls the Mean Depth of the PBL?, *J. Clim.*,
724 18, 3157–3172, 2005.

725 Merlivat, L. and Jouzel, J.: Global Climatic Interpretation of the Deuterium-Oxygen 18
726 Relationship for Precipitation, *J. Geophys. Res.*, 84, 5029–5033, 1979.

727 Monteith, J. L.: Evaporation and environment, *Symposia of the Society for Experimental
728 Biology*, 19, 205–224, 1965.

729 Noone, D., Galewsky, J., Sharp, Z. D., Worden, J., Barnes, J., Baer, D., Bailey, A., Brown, D.
730 P., Christensen, L., Crosson, E., Dong, F., Hurley, J. V., Johnson, L. R., Strong, M., Toohey,
731 D., Van Pelt, A. and Wright, J. S.: Properties of air mass mixing and humidity in the
732 subtropics from measurements of the D/H isotope ratio of water vapor at the Mauna Loa
733 Observatory, *J. Geophys. Res.*, 116, D22113, doi:10.1029/2011JD015773, 2011.

Supprimé: Iannone, R. Q., D. Romanini, O. Cattani, H. A. J. Meijer, and E. R. Th. Kerstel., Water isotope ratio ($d2H$ and $d18O$) measurements in atmospheric moisture using an optical feedback cavity enhanced absorption laser spectrometer, *J. Geophys. Res.*, 115, D10111, doi:10.1029/2009JD012895, 2010. .

- 734 Noone, D.: Pairing Measurements of the Water Vapor Isotope Ratio with Humidity to Deduce
 735 Atmospheric Moistening and Dehydration in the Tropical Midtroposphere, *J. Clim.*, 25,
 736 4476–4494, doi:10.1175/JCLI-D-11-00582.1, 2012.
- 737 Noone, D. C. Risi, A. Bailey, M. Berkelhammer, D.P. Brown, N. Buening, S. Gregory, J.
 738 Nusbaumer, D. Schneider, J. Sykes, B. Vanderwende, J. Wong, Y. Meillier, and D. Wolfe,
 739 2013: Determining water sources in the boundary layer from tall tower profiles of water vapor
 740 and surface water isotope ratios after a snowstorm in Colorado. *Atmos. Chem. Phys.*, 13,
 741 1607-1623, doi:10.5194/acp-13-1607-2013, 2013.
- 742 Ohmura, A. and Wild, M.: Is the Hydrological Cycle Accelerating?, *Science*, 298, 1345–
 743 1346, doi:10.1126/science.1078972, 2002.
- 744 Pfahl, S. and Wernli, H.: Air parcel trajectory analysis of stable isotopes in water vapor in the
 745 eastern Mediterranean, *J. Geophys. Res.*, 113, D20104, doi:10.1029/2008JD009839, 2008.
- 746 Risi, C., Noone, D., Worden, J., Frankenberg, C., Stiller, G., Kiefer, M., Funke, B., Walker,
 747 K., Bernath, P., Schneider, M., Wunch, D., Sherlock, V., Deutscher, N., Griffith, D.,
 748 Wennberg, P. O., Strong, K., Smale, D., Mahieu, E., Barthlott, S., Hase, F., Garcia, O.,
 749 Notholt, J., Warneke, T., Toon, G., Sayres, D., Bony, S., Lee, J., Brown, D., Uemura, R. and
 750 Sturm, C.: Process-evaluation of tropospheric humidity simulated by general circulation
 751 models using water vapor isotopologues: 1. Comparison between models and observations, *J.*
 752 *Geophys. Res.*, 117, D05303, doi:10.1029/2011JD016621, 2012.
- 753 Risi, C., Noone, D., Frankenberg, C. and Worden, J.: Role of continental recycling in
 754 intraseasonal variations of continental moisture as deduced from model simulations and water
 755 vapor isotopic measurements, *Water Resour. Res.*, 49, 4136–4156, doi:10.1002/wrcr.20312,
 756 2013.
- 757 Roderick, M. L. and Farquhar, G. D.: The Cause of Decreased Pan Evaporation over the Past
 758 50 Years, *Science*, 298, 1410–1411, doi:10.1126/science.1075390, 2002.
- 759 Roderick, M. L., Rotstayn, L. D., Farquhar, G. D. and Hobbins, M. T.: On the attribution of
 760 changing pan evaporation, *Geophys. Res. Lett.*, 34, L17403, doi:10.1029/2007GL031166,
 761 2007.
- 762 Salati, E., Dall'Olio, A., Matsui, E., Gat, J.R.: Recycling of water in the Amazon Basin: An
 763 isotopic study, *Water Resources Research*, 15, 1250-1258, 1979.
- 764 Schmidt, M., Maseyk, K., Lett, C., Biron, P., Richard, P., Bariac, T. and Seibt, U.:
 765 Concentration effects on laser-based $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements and implications for the
 766 calibration of vapour measurements with liquid standards, *Rapid Commun. Mass Spectrom.*,
 767 24, 3553–3561, doi:10.1002/rcm.4813, 2010.
- 768 Steen-Larsen, H. C., Johnsen, S. J., Masson-Delmotte, V., Stenni, B., Risi, C., Sodemann, H.,
 769 Balslev-Clausen, D., Blunier, T., Dahl-Jensen, D., Ellehøj, M. D., Falourd, S., Grindsted, A.,
 770 Gkinis, V., Jouzel, J., Popp, T., Sheldon, S., Simonsen, S. B., Sjolte, J., Steffensen, J. P.,
 771 Sperlich, P., Sveinbjörnsdóttir, A. E., Vinther, B. M. and White, J. W. C.: Continuous

Supprimé: (80-.)

Supprimé: (80-.)

- 772 monitoring of summer surface water vapor isotopic composition above the Greenland Ice
773 Sheet, *Atmos. Chem. Phys.*, 13, 4815–4828, doi:10.5194/acp-13-4815-2013, 2013.
- 774 Steen-Larsen, H. C., Sveinbjörnsdóttir, A. E., Peters, A. J., Masson-Delmotte, V., Guishard,
775 M. P., Hsiao, G., Jouzel, J., Noone, D., Warren, J. K. and White, J. W. C.: Climatic controls
776 on water vapor deuterium excess in the marine boundary layer of the North Atlantic based on
777 500 days of in situ, continuous measurements, *Atmos. Chem. Phys.*, 14, 7741–7756,
778 doi:10.5194/acp-14-7741-2014, 2014.
- 779 Sturm, K., Hoffmann, G., Langmann, B. and Stihler, W.: Simulation of $\delta^{18}\text{O}$ in precipitation
780 by the regional circulation model REMOiso, *Hydrol. Process.*, 19, 3425–3444,
781 doi:10.1002/hyp.5979, 2005.
- 782 Sturm, P. and Knohl, A.: Water vapor $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurements using off-axis integrated
783 cavity output spectroscopy, *Atmos. Meas. Tech.*, 3, 67–77, 2010.
- 784 Sun, S., Meng, P., Zhang, J., Wan, X., Zheng, N. and He, C.: Partitioning oak woodland
785 evapotranspiration in the rocky mountainous area of North China was disturbed by foreign
786 vapor, as estimated based on non-steady-state ^{18}O isotopic composition, *Agric. For.*
787 *Meteorol.*, 184, 36–47, doi:10.1016/j.agrformet.2013.08.006, 2014.
- 788 Sunmonu, 'Niyi, Muramoto, K., Kurita, N., Yoshimura, K. and Fujiyoshi, Y.: Characteristics
789 of Seasonal Variation of Near-Surface Water Vapor D/H Isotope Ratio Revealed by
790 Continuous in situ Measurement in Sapporo, Japan, *SOLA*, 8, 5–8, doi:10.2151/sola.2012-
791 002, 2012.
- 792 Tremoy, G., Vimeux, F., Cattani, O., Mayaki, S., Souley, I. and Favreau, G.: Measurements
793 of water vapor isotope ratios with wavelength-scanned cavity ring-down spectroscopy
794 technology: new insights and important caveats for deuterium excess measurements in
795 tropical areas in comparison with isotope-ratio mass spectrometry., *Rapid Commun. mass*
796 *Spectrom.*, 25, 3469–3480, doi:10.1002/rcm.5252, 2011.
- 797 Tremoy, G., Vimeux, F., Mayaki, S., Souley, I., Cattani, O., Risi, C., Favreau, G. and Oi, M.:
798 A 1-year long $\delta^{18}\text{O}$ record of water vapor in Niamey (Niger) reveals insightful atmospheric
799 processes at different timescales, *Geophys. Res. Lett.*, 39, L08805,
800 doi:10.1029/2012GL051298, 2012.
- 801 Tuinenburg, O. A., Hutjes, R. W. A. and Kabat, P.: The fate of evaporated water from the
802 Ganges basin, *J. Geophys. Res.*, 117, D01107, doi:10.1029/2011JD016221, 2012.
- 803 Uemura, R., Matsui, Y., Yoshimura, K., Motoyama, H., and Yoshida, N.: Evidence of
804 deuterium excess in water vapor as an indicator of ocean surface conditions, *J. Geophys. Res.*,
805 113, D19114, doi:10.1029/2008JD010209, 2008.
- 806 [Vallet-Coulomb, C., Gasse, F. and Sonzogni, C.: Seasonal evolution of the isotopic
807 composition of atmospheric water vapour above a tropical lake : Deuterium excess and
808 implication for water recycling. *Geochim. Cosmochim. Acta*, 72, 4661–4674,
809 doi:10.1016/j.gca.2008.06.025, 2008.](#)

Supprimé: Vallet-Coulomb, C., Gasse, F. and Sonzogni, C.: Seasonal evolution of the isotopic composition of atmospheric water vapour above a tropical lake : Deuterium excess and implication for water recycling, *Geochim. Cosmochim. Acta*, 72, 4661–4674, doi:10.1016/j.gca.2008.06.025, 2008.

- 810 Van der Ent, R. J., Savenije, H. H. G., Schaefli, B. and Steele-Dunne, S. C.: Origin and fate of
811 atmospheric moisture over continents, *Water Resour. Res.*, 46, W09525,
812 doi:10.1029/2010WR009127, 2010.
- 813 Wang, L., Caylor, K. K., Villegas, J. C., Barron-Gafford, G. A., Breshears, D. D. and
814 Huxman, T. E.: Partitioning evapotranspiration across gradients of woody plant cover:
815 Assessment of a stable isotope technique, *Geophys. Res. Lett.*, 37, L09401,
816 doi:10.1029/2010GL043228, 2010.
- 817 Wang, L., Niu, S., Good, S. P., Soderberg, K., McCabe, M. F., Sherry, R. A., Luo, Y., Zhou,
818 X., Xia, J. and Caylor, K. K.: The effect of warming on grassland evapotranspiration
819 partitioning using laser-based isotope monitoring techniques, *Geochim. Cosmochim. Acta*,
820 111, 28–38, doi:10.1016/j.gca.2012.12.047, 2013.
- 821 Wassenaar, L. I., Ahmad, M., Aggarwal, P., van Duren, M., Pölsenstein, L., Araguas, L. and
822 Kurttas, T.: Worldwide proficiency test for routine analysis of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in water by
823 isotope-ratio mass spectrometry and laser absorption spectroscopy., *Rapid Commun. mass*
824 *Spectrom.*, 26, 1641–1648, doi:10.1002/rcm.6270, 2012.
- 825 Welp, L. R., Lee, X., Griffis, T. J., Wen, X.-F., Xiao, W., Li, S., Sun, X., Hu, Z., Val Martin,
826 M. and Huang, J.: A meta-analysis of water vapor deuterium-excess in the midlatitude
827 atmospheric surface layer, *Global Biogeochem. Cycles*, 26, GB3021,
828 doi:10.1029/2011GB004246, 2012.
- 829 Wen, X.-F., Zhang, S.-C., Sun, X.-M., Yu, G.-R. and Lee, X.: Water vapor and precipitation
830 isotope ratios in Beijing, China, *J. Geophys. Res.*, 115, D01103, doi:10.1029/2009JD012408,
831 2010.
- 832 Wen, X.-F., Lee, X., Sun, X.-M., Wang, J.-L., Hu, Z.-M., Li, S.-G. and Yu, G.-R.: Dew water
833 isotopic ratios and their relationships to ecosystem water pools and fluxes in a cropland and a
834 grassland in China, *Oecologia*, 168, 549–561, doi:10.1007/s00442-011-2091-0, 2012.
- 835 Werner, M., Langebroek, P. M., Carlsen, T., Herold, M. and Lohmann, G.: Stable water
836 isotopes in the ECHAM5 general circulation model: Toward high-resolution isotope modeling
837 on a global scale, *J. Geophys. Res.*, 116, D15109, doi:10.1029/2011JD015681, 2011.
- 838 Williams, D. G., Cable, W., Hultine, K., Hoedjes, J. C. B., Yopez, E. A., Simonneaux, V., Er-
839 Raki, S., Boulet, G., de Bruin, H. A. R., Chehbouni, A., Hartogensis, O. K. and Timouk, F.:
840 Evapotranspiration components determined by stable isotope, sap flow and eddy covariance
841 techniques, *Agric. For. Meteorol.*, 125, 241–258, doi:10.1016/j.agrformet.2004.04.008, 2004.
- 842 Worden, J., Noone, D. and Bowman, K.: Importance of rain evaporation and continental
843 convection in the tropical water cycle, *Nature*, 445, 528–32, doi:10.1038/nature05508, 2007.
- 844 [Yakir, D. and Wang, X.-F., Fluxes of CO₂ and water between terrestrial vegetation and the](#)
845 [atmosphere estimated from isotope measurements, *Nature*, 380, 515-517, 1996.](#)
- 846 Yakir, D. and Sternberg, L. da S. L.: The use of stable isotopes to study ecosystem gas
847 exchange, *Oecologia*, 123, 297–311, 2000.

- 848 Yamanaka, T. and Shimizu, R.: Spatial distribution of deuterium in atmospheric water vapor:
849 Diagnosing sources and the mixing of atmospheric moisture, *Geochim. Cosmochim. Acta*, 71,
850 3162–3169, doi:10.1016/j.gca.2007.04.014, 2007.
- 851 Yepez, E. A., Williams, D. G., Scott, R. L. and Lin, G.: Partitioning overstory and understory
852 evapotranspiration in a semiarid savanna woodland from the isotopic composition of water
853 vapor, *Agric. For. Meteorol.*, 119, 53–68, doi:10.1016/S0168-1923(03)00116-3, 2003.
- 854 Zhang, S., Wen, X., Wang, J., Yu, G. and Sun, X.: The use of stable isotopes to partition
855 evapotranspiration fluxes into evaporation and transpiration, *Acta Ecol. Sin.*, 30, 201–209,
856 doi:10.1016/j.chnaes.2010.06.003, 2010.
- 857 Zhang, S., Sun, X., Wang, J., Yu, G. and Wen, X.: Short-term variations of vapor isotope
858 ratios reveal the influence of atmospheric processes, *J. Geogr. Sci.*, 21, 401–416,
859 doi:10.1007/s11442-011-0853-6, 2011.

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863 Table 1. Isotopic compositions of laboratory standards (δ_{LS}), and statistics on raw
 864 measurements from all calibrations (average and standard deviation of δ_{raw} from 40 data
 865 between 20 July to 24 August 2011).
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		δ_{LS} (‰ vs VSMOW)	Average and standard deviation of δ_{raw} (‰)	
Standard 1	$\delta^{18}O$	-17.12	-13.89	0.19
	δD	-133.3	-152.6	2.0
Standard 2	$\delta^{18}O$	-7.85	-4.85	0.11
	δD	-53.5	-71.1	1.5
Standard 3	$\delta^{18}O$	0.68	3.41	0.08
	δD	3.7	-12.8	1.8

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869 | Table 2. Evaluation of the stability of the calibrations in water vapour concentration and
 870 | isotopic composition, with mean slope and mean intercept ± 1 standard deviation obtained for
 871 | $\delta^{18}\text{O}$ and δD with n calibrations performed from 20 July to 24 August 2011.
 872

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	$\delta^{18}\text{O}$	δD
Water <u>vapour</u> concentration		
Slope	$-0.16 \cdot 10^{-4} \pm 0.13 \cdot 10^{-4}$	$6.08 \cdot 10^{-4} \pm 0.99 \cdot 10^{-4}$
Intercept	-13.68 ± 0.25	-165.4 ± 2.0
R^2 (n=23)	$0.26 \leq R^2 \leq 1.00$	$0.89 \leq R^2 \leq 0.99$
Isotopic composition		
Slope	1.03 ± 0.01	0.98 ± 0.01
Intercept	-2.83 ± 0.07	16.3 ± 1.7
R^2 (n=40)	1.00	1.00

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874 Table 3. Results of Standard 2 measurements ($\delta_{\text{std2-m}}$) normalized to the VSMOW2-SLAP2
 875 scale by using Standards 1 and 3 as working standards, following the IAEA Reference Sheet
 876 (IAEA, 2009). Statistics are performed from the set of 40 calibrations. Standard deviation
 877 provides the reproducibility, and the root mean square deviation from the known value
 878 (RMSE) provides the accuracy of liquid measurements.

879

	$\delta^{18}\text{O}$	δD	d
	(‰ VSMOW)	(‰ VSMOW)	(‰)
Average of $\delta_{\text{std2-m}}$	-7.82	-53.4	9.16
Standard deviation	0.117	0.89	1.29
RMSE	0.121	0.89	1.30

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882 Table 4. Determination coefficients (R^2) and slopes (S) of linear correlations between daily
 883 means of water vapour composition ($\delta^{18}\text{O}$, δD , d) and air temperature (T_a), mixing ratio (q),
 884 relative humidity at air temperature (RH_a) and relative humidity at water surface temperature
 885 (RH_s).

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	$\delta^{18}\text{O}$ (‰)		δD (‰)		d_v (‰)	
	R^2	S	R^2	S	R^2	S
T_a (°C)	0.30	+0.54	0.27	+3.48	0.20	-0.88
q ($\text{mmol}\cdot\text{mol}^{-1}$)	0.72	+0.38	0.62	+2.39	0.54	-0.66
RH_a (%)	0.64	+0.13	0.55	+0.80	0.51	-0.23
RH_s (%)	0.33	+0.13	0.31	+0.83	0.19	-0.19

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888 Table 5. Number of days (n) associated with the different origins of air masses (Figure 1).
 889 Corresponding mean values of $\delta^{18}\text{O}$, δD , deuterium excess (d), air temperature (T), mixing
 890 ratio (q), relative humidity (RH), wind speed (V) and potential evapotranspiration (PET)
 891 measured in the experimental site.
 892

	North Atlantic [310°-360°]	Mediterranean [110°-220°]	Bay of Biscay [220°-310°]
n	10	13	13
$\delta^{18}\text{O}$ (‰)	-15.83	-13.13	-14.90
δD (‰)	-103.5	-86.5	-96.3
d (‰)	23.2	18.6	22.9
T_a (°C)	21.6	23.3	22.3
q (mmol.mol ⁻¹)	15.0	21.8	18.0
RH (%)	59.5	78.5	68.1
V (m.s ⁻¹)	2.0	0.7	1.6
PET (mm.day ⁻¹)	5.8	3.8	4.9

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895 Figure 1. Location of the experimental site (star) in Camargue (Rhône River Delta), 170m
896 from the Vaccarès lagoon and 12km from the Mediterranean Sea. Coloured arrows represent
897 the three main origins and trajectories of air masses affecting the study site, (1) North
898 Atlantic, (2) Mediterranean and (3) Bay of Biscay.

899

900 Figure 2. Raw $\delta^{18}\text{O}$ and δD of our three laboratory liquid standards measured at various water
901 vapour concentrations. Error bars are smaller than the symbols. Linear regressions within the
902 concentration range encountered in Camargue during the field experiment and associated
903 slopes and determination coefficients are shown.

Supprimé: vapor

904

905 Figure 3. Hourly time series of air temperature (T), mixing ratio (q), $\delta^{18}\text{O}$, δD , deuterium
906 excess (d) from 20 July to 24 August 2011 at the experimental site according to air mass
907 origin (see Figure 1). Grey dots are δ_v and d values calculated from the isotopic equilibrium
908 with precipitation.

Supprimé: mean values

Supprimé: d_v

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910 Figure 4. Hourly daytime and night-time isotopic composition of atmospheric water vapour
911 according to air mass origins. For reference, the GMWL and LMWL are also plotted.

Supprimé: day-time

Supprimé: vapor

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913 Figure 5. Average daily cycles of $\delta^{18}\text{O}$, δD , deuterium excess (d), relative humidity at surface
914 (RH_s) and air (RH_a , grey symbols) temperature, surface (T_s) and air (T_a , grey symbols)
915 temperature, mixing ratio (q) and planetary boundary layer height (PBLH) calculated from 20
916 July to 24 August 2011 according to the three air mass origins. Grey shading indicates
917 standard deviation of each average value.

Supprimé: 24-hour average values

918

919 Figure 6. Relationships between hourly average values of δ_v and $1/q$ over a daily cycle
920 according to the two main air mass origins, and corresponding linear regressions for the
921 period of q increase (see text). Squares indicate the isotopic composition of the local end-
922 member (δ_E) calculated for a mixing ratio corresponding to saturation at the water surface
923 temperature.

Supprimé: 24-

Supprimé: vapor

Mis en forme: Indice

924

925 | Figure 7. Hourly average values of δD versus $\delta^{18}O$ over a daily cycle, according to the two
926 | main air mass origins, corresponding linear regressions for the period of q increase (see text),
927 | and calculated local end-member (δ_E). For reference, the LMWL is also plotted.
928 |

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