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

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Abstract

Stable isotopes of the water vapor represent a powerful tool for tracing atmospheric vapor origin and mixing processes. Laser spectrometry recently allowed high time resolution measurements, but despite an increasing number of experimental studies, there is still a need for a better understanding of the main drivers of isotopic signal variability at different time scales. We present results of in situ measurements of $\delta^{18}O$ and δD during 36 consecutive days in summer 2011 in atmospheric vapor of a Mediterranean coastal wetland exposed to high evapotranspiration (Camargue, Rhône River delta, France). A calibration protocol was tested and instrument stability was analysed over the period. The mean composition of atmospheric vapor during the campaign is $\delta^{18}O$=-14.66‰ and δD=-95.4‰, with δ_v data plotting clearly above the local meteoric water line, and an average deuterium excess (d_v) of 21.9‰. 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 ($\delta^{18}O$=-15.83‰, δD=-103.5‰) compared to Mediterranean air masses ($\delta^{18}O$=-13.13‰, δD=-86.5‰). There is also a clear separation between d_v 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 diurnal d_v variations are more important than day-to-day differences, an hourly time scale analysis is necessary to interpret the main drivers of d_v variability. 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. Diurnal fluctuations are driven by 1) the influence of local evaporation, culminating during day-time, and leading to an increase in absolute water vapor concentration associated to a δ_v enrichment and d_v increase; 2) vertical air mass redistribution when the PBL vanishes in the evening, leading to a d_v decrease, and 3) dew formation during the night, producing a δ_v depletion with d_v remaining stable. Based on a two-component mixing model, we calculate the average composition of the local vapor that produces the day-time increase in d_v, and found higher d_v for the local vapor composition under North Atlantic air mass conditions, consistent with lower humidity conditions. In addition, we show that the stronger advection rate that prevails under Northern conditions dilutes the contribution of local vapor to the ambient moisture, which indicates that regional vapor also carries a higher d_v under Northern conditions. This isotopic mass balance approach is proposed as a framework for deciphering regional and local influences.

1 Introduction

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

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

Laser spectrometers recently opened the door towards the high temporal resolution analysis of δ_v variations, which was not possible with the traditional cold trap method. Whereas cryogenic trapping provides grab samples generally averaging a couple of hours, laser spectrometry performs continuous high frequency (up to ~1 Hz) measurements of δ_v (Kurita et al., 2012). This technology offers new insights into processes that affect the isotopic composition of atmospheric water vapor and the number of studies based on continuous ground level isotope measurements over multi-week periods is continuously increasing, either using Tunable Diode Laser (TDL) (Lee et al., 2006; Wen et al., 2010; Griffis et al., 2011; Welp et al., 2012; Wen et al., 2012), Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) (Sturm and Knohl, 2010; Sunmonu et al., 2012; Farlin et al., 2013; Steen-Larsen et al., 2013) or Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-CRDS) (Galewsky et al., 2011; Noone et al., 2011; Tremoy et al., 2012; Steen-Larsen et al., 2013, 2014). Among these experiments are some low latitude studies which have focused on the tracing of tropical or sub-tropical convective activity in West Africa (Tremoy et al., 2012) or in South America (Galewsky et al., 2011). In mid latitudes (Noone et al., 2011; Farlin et al., 2013), or high latitudes (Steen-Larsen et al., 2013), several studies have explored atmospheric mixing processes at different time scales. Isotopes have also been used for partitioning evapotranspiration into plant transpiration and direct evaporation, as the associated fractionations are different (Yakir and Sternberg, 2000; Lai et al., 2006; Wang et al., 2010; Griffis et al., 2011; Sun et al., 2014), for a better understanding of the role of ecosystems in the hydrological cycle in the context of climate change (Wang et al., 2013).

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

In this paper, we provide results obtained in Camargue on 36 consecutive days during summer 2011, using WS-CRDS technology. The Camargue region is emblematic of Mediterranean wetlands, with important water inflow requirements and strong evaporation losses, making them highly sensitive to climate change and human pressures on water resource. Our experimental site is located in the center of Camargue, close to the main lagoon (Vaccarès lagoon, 65 km^2). Considering the location of the site, and the important availability of open water in the surroundings, we expect a dominant contribution of evaporation upon transpiration fluxes. This study will provide the opportunity to investigate how local evaporation combines and interact with the other regional vapor sources. We will focus on identifying the main drivers of deuterium excess variability at different time scales, and explore the relevance of using either relative humidity, as an indicator of evaporation conditions, or specific humidity (mixing ratio) as a proxy of mixing between different vapor sources. Before analysing our results, we present technical aspects of measurement calibration and validation. We then analyse the day-to-day variations of δ_v and d_v in relation to climatic parameters and the air mass back trajectories. Finally, average hourly variations are explored and we interpret the typical daily cycles according to the main regional meteorological conditions in order to depict their driving factors and the influence of local processes.

2 Data acquisition

2.1 Protocols

Continuous in situ measurements of the isotopic composition of atmospheric water vapor ($\delta^{18}O$ and δD) were performed during summer 2011 between 20 July and 24 August, at 1.75m height and approximately 170m from the East border of the Vaccarès lagoon (Figure 1), using Wavelength-Scanned Cavity Ring-Down Spectroscopy (WS-CRDS). The instrument we use is the Picarro L1102-i isotopic liquid water and water vapor analyser (Picarro Inc., Sunnyvale, California, USA), which measures the isotopic composition of atmospheric water vapor every 5 to 7 seconds. Installed in an air-conditioned room, the analyser is connected to an outside air intake. As water vapor may be sticky on the walls of any tubing, a bypass configuration is used to bring the air in quickly, at a rate of 6L.min^{-1} (with a Laboport vacuum pump N86 KN.18) through PVC tubing, in order to minimise wall effects that lead to fractionation in the inlet. The analyser then subsamples this air at a rate lower than 0.04L.min^{-1}.

Calibration of laser measurements is performed according to liquid laboratory standards, and a three -way valve allows switching between the introduction of ambient air and vapor from the liquid sample vaporizer (vaporization module V1102-i adjusted to 110°C for flash vaporization to avoid fractionation). We used three laboratory standards whose isotopic spans a range of values including the composition expected in the atmosphere of the Camargue (Table 1). 1.8µL of water standards are introduced is injected into the vaporizer using an autosampler (CTC Analytics LEAP Technologies HTC PAL autosampler) with a SGE 5µL syringe. We used synthetic air as the dry carrier gas (water content <45ppmv) delivered at a pressure of 2.5±0.5psi. The analyser takes about nine minutes to perform approximately 40 measurements per injection, and these results are then averaged by the software. Between each injection, the syringe is cleaned with 1-methyl-2-pyrrolidinone (NMP) solvent wash. Our laboratory successfully participated in the IAEA 2011 proficiency test on routine analysis of $\delta^{18}O$ and δD in liquid water (Wassenaar et al., 2012).

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

Gaps in time series correspond to calibration periods, but may also reflect accidental power cuts or data eliminated during episodes of condensation in the tubing. This latter problem was detected thanks to the use of transparent air tubing, and was easily recognizable a posteriori through the abnormally smooth shape of the water vapor concentration curve. A heating cable was then used to avoid any condensation such as may occur when a negative temperature gradient exists between the sampling point and the inlet of the analyser.

2.2 Dependence on water vapor concentration

It has been shown that the dependence of WS-CRDS isotopic measurements on water vapor concentration is instrument-dependent (Tremoy et al., 2011). The concentration dependence of our instrument, evaluated for a large range of concentrations (Figure 2), showed a linear response in the range of water vapor concentration measured in the atmosphere of the Camargue (from 9000ppmv to 28000ppmv), with the relationship deviating slightly from the linear trend at very low and high water vapor concentrations. For $\delta^{18}O$ of standards 2 and 3 there is no concentration effect, but a small dependence did appear for the more depleted standard (-0.33‰.10000ppmv^{-1}; R^2=0.75). For δD, we found significant regression coefficients (R^2=0.98, 0.99 and 1.00 for standards 1, 2 and 3 respectively), and the slope of the dependence was only slightly different between standards (between 7.8 and 8.1‰.10000ppmv^{-1}).

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

$$\delta_{reference} = \delta_{observed} + m \cdot \left(w_{reference} - w_{observed} \right) \qquad (1)$$

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

2.3 Instrument stability

To evaluate the long-term stability of our instrument, statistics were calculated on raw delta values measured on our three standards during the entire measurement campaign (Table 1). Results show that the long-term variability is very low, but a regular calibration is nevertheless performed. Variability of both calibrations (for water vapor concentration and isotopic composition) is shown in Table 2. For $\delta^{18}O$, the calibration for concentration appears highly variable but often flat (no concentration effect), resulting in a linearity which is not always significant ($0.26 \leq R^2 \leq 1.00$). Thus, $\delta^{18}O$ was corrected only when the concentration dependence was significant. For δD, the regression is slightly variable in the long-term, and its linearity is always significant ($0.89 \leq R^2 \leq 0.99$). For daily calibration in isotopic composition (normalisation to the VSMOW2-SLAP2 scale), we used a three-point calibration, which allows to check for the linearity of the calibration. Linear regressions between raw measured values and absolute standard compositions are established as follows for $\delta^{18}O$ and δD:

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

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

3 Local atmospheric data

Hourly air temperature and relative humidity were measured at the study site. Hourly wind speed and daily PET (Potential Evapotranspiration calculated from the Penman-Monteith formula, Monteith, 1965) were obtained from a meteorological station located 400m far from the site of isotopic measurements. In addition, surface temperature was also measured in the main pond of the Vaccarès lagoon system at hourly time-step. Backward three-dimensional trajectories were computed for each individual day with the Internet-based NOAA HYSPLIT Trajectory Model (http://ready.arl.noaa.gov/HYSPLIT.php), using GDAS (Global Data Assimilation System) meteorological data. The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is a complete system which allows computing simple air parcel trajectories. Trajectories were parameterized to end up at the station location at 1200 UTC, at three heights of 50, 100 and 500 meters above ground level, with a total back run time long enough to get back to the oceanic source (maximum of 144 hours). Planetary boundary layer heights were obtained from GDAS meteorological data (3-hour time step). They were extracted and interpolated to our specific station using the MeteoInfo software (www.meteothinker.com).

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

4 Results and discussion

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

In measured atmospheric vapor, substantial day-to-day variations of δ_v are observed, while d_v presents high hourly variations (Figure 3). In order to explore the relevant time scales for interpreting isotopic data in terms of synoptic and mesoscale meteorology versus local influences, we first analyse the relations of our data to daily climatic variables and air mass origins. Then, we focus on average diurnal variations for identifying the local influences.

4.1 Correlations between isotope data and local climatic parameters

Quite good correlations are found between daily values of δ_v and local climatic parameters (Table 4), the best fit being with the mixing ratio q, (R^2=0.72 and 0.62 for $\delta^{18}O$ and δD respectively). Such a correlation could result from the case of simple Rayleigh rainout processes, where condensation phases progressively remove water from the atmosphere and deplete the remaining atmospheric vapor in heavy isotopes (Dansgaard, 1964; Lee et al., 2006; Wen et al., 2010). The progressive rainout follows a temperature decrease, and should also result in a correlation between δ_v and T, and subsequently between rainfall isotope content (δ_p) and T, which has led to the establishment of the isotopic thermometer (Dansgaard, 1964; Jouzel et al., 1997). Our data show a relation between δ_v and T (Table 4, Figure 3) close to the isotopic thermometer: $\Delta\delta^{18}O/\Delta T$=0.53‰.°$C^{-1}$ (Jouzel et al., 1997), but the correlation is relatively poor (R^2=0.30), indicating more complex processes, as was observed during a long-term German survey in which δ_v–T correlation was degraded during summer because of the admixture of vapor originating from plant evapotranspiration (Jacob and Sonntag, 1991). Since the correlation between δ_v and q is much stronger than the δ_v–T correlation, it indicates a mixing between air masses characterized by different vapor concentrations as could result from different marine origins, and/or from the addition of continental vapor into the atmosphere.

With respect to deuterium excess, we found that q is also the best predictor of d_v variations at a daily time-step (R^2=0.54, Table 4). In addition, we observed a correlation between d_v and RH_a (R^2=0.51), consistent with Welp et al. (2012), but the correlation becomes very low (R^2=0.19) when using relative humidity at surface temperature (RH_s). The significance of deuterium excess in terms of a proxy for the conditions at the vapor sources comes from the fact that it is determined by the isotopic fractionation that occurs during evaporation, and more precisely by its variable kinetic component, which mainly depends on relative humidity (Craig and Gordon, 1965; Gonfiantini, 1986; Pfahl et Wernli, 2008; Uemura et al., 2008). However, relative humidity is only relevant for characterizing evaporation conditions if reported at surface temperature. In this case it represents the vapor concentration gradient between water and air, which controls the kinetic fractionation. Starting from a value around d_v=0‰ in ocean water, the kinetic fractionation associated to initial seawater evaporation produces an increase in d_v in oceanic vapor inversely related to humidity conditions (Merlivat and Jouzel, 1979; Armengaud et al., 1998; Pfahl et Wernli 2008; Uemura et al 2008; Jouzel et al., 2013; Steen-Larsen et al., 2013). During the air mass trajectory over land, d_v may be further increased by the addition of vapor of continental origin (Gat and Matsui, 1991, Gat et al., 1994; Angert et al., 2008; Lai and Ehleringer, 2011; Welp et al., 2012). This "secondary" vapor is also expected to carry a d_v inversely related to humidity conditions at the vapor source (Aemisseger et al., 2014). However, the lack of correlation between d_v and RH_s in our data, whilst the d_v-q correlation is stronger, suggests that mixing processes between air masses characterized by different vapor origins and concentrations have weakened the d_v and RH_s relation, as was the case for the δ_v-q correlation.

Since it is hardly modified by equilibrium condensation, d_v can be considered as a conservative tracer of vapor sources during mixing processes. Nevertheless, the conservative behaviour of d_v during rainout is perturbed by the non-linearity in the definition of deuterium excess: the delta-notation approximation induces a small shift in d_v when there is a large decrease in δ^{18}O and δD (Gat et al., 1996; Angert et al., 2008; Welp et al., 2012). In the observed range of δ^{18}O (from -11 to -18‰), we have estimated this effect to induce a 2.5‰ increase in d_v, while the substantial variations in d_v observed in our daily data are significantly higher (from 15 to 26‰), allowing the use of d_v as a tracer of different vapor pools.

4.2 Regional isotopic signatures

In order to examine the link between the isotopic characteristics of vapor and the air mass trajectories since its oceanic origin, data were classified, on a daily basis, following the three main regional features schematically represented in Fig. 1. Corresponding hourly data are scattered in the δ^{18}O-δD plot distinctly above the local meteoric water line (LMWL, Figure 4), and show isotopically depleted compositions for air masses coming from the North Atlantic, while air masses coming from the Mediterranean Sea display isotopically enriched vapor (Table 5, Figure 4). For air masses coming from the Bay of Biscay, hourly data encompass the entire isotopic range. Local climatic data associated with the three meteorological situations reflect synoptic weather conditions related to origin of air masses. Air masses coming from the North Atlantic are associated with cold, dry and strong winds, while those from the Mediterranean are associated on the contrary with warm, wet and light winds (Table 5). The Bay of Biscay is an intermediate situation. It thus appears that the greater the distance over land (Figure 1), the more depleted is δ_v. The northern trajectory corresponds to a "Mistral" situation: a typical cold, dry and strong north-northwest wind that affects the north of the occidental Mediterranean basin 130 days a year on average. The air mass is gradually dried out by rainout processes over land and accelerated in the Rhône River Valley and acquires a depleted isotopic signature. On the contrary, an air mass travelling over the Mediterranean Sea with the slight thermal wind or sea breeze coming from the South is moistened and acquires and maintains an enriched isotopic signature.

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

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

4.3 Analysis of average daily cycles

In order to observe the diurnal variations suggested by the night-day separation, 24-hour average values of isotopic and climatic data are plotted for the three air mass origins (Figure 5). A well-pronounced cyclicity appears for d_v in each meteorological condition. For Bay of Biscay origins, the average d_v cycle is very similar to the North Atlantic conditions, with larger standard deviations, reflecting a more variable climatic situation. For Mediterranean conditions, the d_v cycle is higher in amplitude than for North Atlantic conditions, and lower in absolute values, especially during the night. The high standard deviations observed during the last hours of the day correspond to calibration periods for which there are fewer data, but may also be due to variations in the timing of the PBL evening transition. The increase in d_v during the morning is mainly associated with a δD increase, while δ^{18}O variations are smoother. Amplitudes of daily isotopic variations are higher for Mediterranean conditions (9.7‰, 16.2‰ and 1.3 ‰ for d_v, δD and δ^{18}O respectively) than for North Atlantic ones (7.0‰, 13.1‰ and 1.1‰ for d_v, δD and δ^{18}O respectively).

From a climatic point of view, we observe high diurnal variations in RH_a, mainly driven by the large amplitude of air temperature variations between night and day (not shown). As discussed above, the significance of relative humidity conditions in terms of evaporation conditions – and deuterium excess control – is only relevant at surface temperature. The variations are smoother for RH_s, and it more or less follows the absolute amount of water (Figure 5). Under Mediterranean conditions, a distinct increase of q occurs in the morning, indicating a net addition of vapor in the atmosphere. Under North Atlantic conditions, the q increase is lower, but still detectable.

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

Day-time processes: contribution of local evaporation

The diurnal increase in d_v is a widely observed feature, which reflects the diurnal variation of the water and air mass balances of the planetary boundary layer. In many studies, it has been attributed to entrainment of free atmosphere into the boundary layer (Lai and Ehleringer, 2011; Zhang et al., 2011; Welp et al., 2012; Berkelhammer et al., 2013). However, it could also be due to the addition of locally evaporated vapor, as was observed by Welp et al. (2012). The direction of vapor concentration changes associated with these dv variations can help to identify which of these two processes dominates the PBL water mass budget. Entrainment brings a dryer air into the PBL, and thus causes a day-time decrease in vapor concentration, while an increase in mixing ratio points to the addition of an evaporation flux. Note that the transpiration component of evapotranspiration is not expected to carry high d_v, as it has the same isotopic composition as the soil water at steady state (Yakir et Wang, 1996; Williams et al., 2004). In addition, the free atmospheric air is characterized by a isotopically lighter vapor (He and Smith, 1999; Bailey et al., 2013; Berkelhammer, et al 2013), and the dominance of day-time entrainment during day-time is generally associated with a δ_v depletion (Lai C.-T. et al., 2006; Lai and Ehleringer, 2011; Tremoy et al., 2012; Bailey et al., 2013; Berkelhammer, et al 2013). Welp et al. (2012), compared six measurement locations and found that both local evapotranspiration and entrainment were involved: in some of their sites, the d_v daily increase was associated with a $\delta^{18}O$ decrease during the early morning due to entrainment of free atmosphere into the boundary layer during convective mixing, while the subsequent slight $\delta^{18}O$ increase came from evapotranspiration. Our data display daytime increases in q, $\delta^{18}O$ and δD (Figure 5), and thus indicates that the addition of surface vapor is the dominant process governing the d_v cyclicity during the day.

Nocturnal processes: dew formation

During the night, the PBL subsidence corresponds to the disappearance of both the surface heat fluxes and entrainment. There is thus no further addition of water vapor to the atmosphere. The large-scale motion becomes dominant and, without changing the total PBL mass, redistributes it horizontally (Medeiros et al., 2005). We can thus interpret the nocturnal isotopic values as representing an average signal, onto which are superimposed day-time fluxes. The tendencies identified at daily time step which are interpreted in terms of regional signature, that is to say, depleted (enriched) δ_v and higher (smaller) d_v under North Atlantic (Mediterranean) conditions, are recovered in night-time values (Table 5, Figure 6). However, the isotopic composition is not constant and follows a gradual depletion during the 20h-6h UTC period, together with a decrease in water concentration and a stable d_v value, which indicates a progressive Rayleigh-condensation process, as was observed by Berkelhammer et al. (2013). The averaged composition of the planetary boundary layer is thus represented by the value measured just after the sunset (20h UTC), when the PBL vanishes and produces a vertical mixing of the atmosphere, and before the influence of dew formation. The d_v values remains high during the night (on average 15,1 ±0,5‰ under Mediterranean conditions and 20.9 ±0,7‰ under North Atlantic conditions), and suggest that the influence of local vapor still affects the average isotopic signal.

4.4 Local isotopic signatures

The concomitant increase of q and d_v during day-time in our average data indicates that the d_v cyclicity is mainly driven by local vapor fluxes. As stated above, the location of the experimental site close to the main lagoon, and the important availability of open water in the surroundings, point to a dominant contribution of evaporation upon transpiration. In order to calculate the local vapor isotopic composition (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 validity of this simple model and the possible contribution of regional advection will then be 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 vapor 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 an isotopically stable background, with an initial mixing ratio q_0 (mmol/mol) and a vapor composition δ_0, the addition of a water vapor amount W_1 (mmol) with a composition δ_1, leads to the following mixing equations:

$$q = q_0 + W_1 \qquad (3)$$

where q is the mixing ratio (mmol/mol) of the resulting atmosphere. Attributing an isotopic composition to each of these vapor pools, the corresponding isotopic mass balance is:

$$\delta_v = (\delta_0 - \delta_1) \cdot \frac{q_0}{q} + \delta_1 \qquad (4)$$

where δ_v is the vapor composition of the resulting atmosphere. In a data set characterising the progressive addition of vapor in a closed system, the δ_v *versus* 1/q relation displays a linear shape, and the composition of the added vapor δ_1 is deduced from the intercept (for $q \rightarrow \propto$). However, in an open atmosphere where water vapor is added through the mixing with a humid air mass, equation (3) becomes:

$$q = xq_0 + (1 - x)q_1 \qquad (5)$$

Where x is the fraction of the initial background air, q_1 is the mixing ratio of the added air mass (mmol/mol), and the corresponding isotopic mass balance is:

$$\delta_v = (\delta_0 - \delta_1) \cdot \frac{xq_0}{q} + \delta_1 \qquad (6)$$

In a δ_v versus 1/q plot, the composition of the added vapor is then deduced for x=0, i.e. by extrapolating the linear trend until $1/q_1$.

The application of this two-component mixing model thus requires the knowledge of the vapor content of the added air. If it comes from open water evaporation, we can use the mixing ratio which corresponds to saturation conditions (Noone, 2011, 2012). 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.

We focus our discussion on the two most contrasted meteorological situations, i.e. Mediterranean and North Atlantic air mass origins. Strong correlations are found between average values of δ_v and 1/q for the period of q increase, i.e 5h-13h UTC for North Atlantic situations and 5h-10h for Mediterranean situations (R^2 values are between 0.85 and 0.96, see Figure 6). The local end-members are calculated for the average value of saturation mixing ratio at the water surface temperature (q_s), during the daily maximum air water concentrations (at 13h UTC or 10h UTC). Uncertainties are determined as resulting from error propagation of the linear model in the whole range of q_s standard deviation. The resulting compositions of local end-members (δ_E) are: $\delta^{18}O$=-12.5‰ (-12.3‰ to -12.9‰); δD=-48‰ (-44‰ to -54‰) for North Atlantic conditions, $\delta^{18}O$=-11.8‰ (-11.0‰ to -12.5‰); δD=-58‰ (-46‰ to -68‰) for Mediterranean conditions (Figure 7). These results show the high deuterium excess values characterizing the surface vapor (d_v= 52‰ ±6‰ for North Atlantic and 37‰ ±5‰ for Mediterranean conditions). Such high values are consistent with the isotopic composition of open water evaporation estimated from the Craig and Gordon model (Craig and Gordon, 1965; Gat et al, 1994). The high d_v of evaporated moisture have made it possible to detect its contribution to regional precipitation (Gat et Matsui, 1991, Gat et al, 1994) or to partition the composition of a vapor flux into evaporation and transpiration (Williams et al., 2004). In our case, these high d_v values confirm that evaporation is largely dominant upon transpiration, and the higher d_v under North Atlantic air mass conditions is consistent with lower RH_s, compared to Mediterranean conditions (Figure 5, Table 5).

As a first attempt, we use this δ_E composition for interpreting the diurnal amplitude of δ_v from a simple isotopic mass balance:

$$\frac{W_E}{W} = \frac{\delta_{v(\max)} - \delta_{v(\min)}}{\delta_E - \delta_{v(\min)}} \qquad (7)$$

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.

The lower amplitude of diurnal variations observed under North Atlantic condition would thus indicate a lower proportion of local vapor, but, compared to the Mediterranean situation, North Atlantic conditions correspond to stronger average potential evapotranspiration rates: 5.8mm.day^{-1} *versus* 3.8mm.day^{-1} (Table 5). This apparent contradiction indicates that the isotopic imprint of local evaporation is diluted by advection, consistently with the high wind speed that prevails under North Atlantic conditions (2.0 m.s^{-1} compared to 0.7 m.s^{-1} for Mediterranean conditions). The local vapor is thus flushed by advection of dry northward air masses, and since this advected vapor may carry a different isotopic signature than the nocturnal background, a simple two-component model is not sufficient to describe the PBL water balance.

We have performed sensitivity analysis to evaluate the impact of a third component on the use of the δ_v-1/q relationship for determining δ_E, considering an advected air mass dryer than local atmosphere (i.e. on the right hand of observed data in Figure 6). The occurrence of regional advection remains compatible with a linear δ_v-1/q trend, but slightly influences the observed slope, and thus, the estimated humid end-member composition: if the advected vapor composition is more enriched than the initial background, it leads to overestimate the δ_E value, and vice-versa. The composition of the advected vapor is isotopically heavier than the 5:00 UTC value, since the nocturnal dew formation induces a depletion of atmospheric vapor. The use of a two-component mixing assumption would therefore lead to overestimate δ_E, and the actual average composition of local vapor is expected to plot between this δ_E estimate and daily maximum measured δ_v (Figure 7).

Nevertheless, this simple mass balance approach can be used as a framework for deciphering the complex regional and local influences affecting δ_v and d_v. In addition, the processes involved in the diurnal isotopic behaviour of atmospheric vapor can be summarized in the $\delta^{18}O$-δD plot, which is a good mean to understand the drivers of d_v variations (Figure 7). The two clusters of average vapor data are distributed along two linear trends defined by the q-increase period of the day, which also meet the calculated value of δ_E. These trends result from the addition of local vapor into the ambient air, but, as discussed above, are also influenced by the input (and flushing) of regional advection. The day-time vapor composition then oscillates, but stays around the maximum δ_v value, until the abrupt shift that occurs at 20:00 UTC, during sunset, consistently for both meteorological situations. The d_v decrease observed when the PBL vanishes corresponds to the vertical mixing of the PBL, as previously stated, and is therefore driven by the mixing with a more regional vapor. The night-time evolution of δ_v is thus slightly shifted closer to the meteoric water line, compared to day-time compositions. The progressive condensation that occurs between 20:00 and 5:00 UTC maintains the δ_v along a regression line roughly parallel to the LMWL.

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

5 Conclusions

Our results showed that daily averages of atmospheric vapor compositions are mainly controlled by synoptic and mesoscale weather conditions, related to air mass origin and trajectory. Cold, dry and strong winds coming from the North bring an isotopically depleted vapor. Inversely, warm, wet and light winds coming from the South bring an isotopically enriched vapor. In all situations, d_v is higher than the global average of 10, and higher than deuterium excess measured in rainfall, both when considering the small rainfall events during the campaign, or the long-term average composition of regional precipitation. Higher d_v is found for Northern air masses (23.2‰) than for Mediterranean air masses (18.6‰), but the amplitude of day-night differences is more important than day-to-day variations, and the drivers of these diurnal variations have to be understood for interpreting the isotopic signal with respect to its relevant spatiotemporal scales. Indeed, a day-time increase in d_v can be caused either by entrainment of free atmospheric air, either by local evaporation, both processes having different spatial significances.

Unlike evaporation, the contribution of free atmospheric air would have induced a decrease in absolute vapor concentration, and our twenty-four hour average data clearly indicate that the diurnal δ_v cycles are essentially driven by local evaporation. Based on the robust alignment of average data in a δ_v-1/q plot for the q-increase periods of the day, we applied a two-component mixing model for estimating the composition of local evaporation (δ_E). This two-component mixing assumption does not account for the influence of regional advection, which modulates the amplitude of diurnal δ_v variations. Sensitivity analysis showed that the error associated with the use of a two-component assumption leads to slightly overestimate the δ_E values, especially under North-Atlantic conditions. Nevertheless, we found higher d_v for the local vapor composition under North Atlantic air mass conditions consistent with lower humidity conditions. In addition, the stronger advection rate that prevails under North-Atlantic conditions suggests that, in this situation, the higher average d_v of water vapor also reflects the signature of regional vapor.

Overall, our data showed that mixing ratio is a better predictor of deuterium excess variations than relative humidity, at both daily and sub-daily time scales, because mixing processes between different vapor sources have weakened the relevance of relative humidity as an indicator of evaporation conditions. At the daily time step, mixing ratio is a proxy of the air mass origin, since there is a huge contrast between water content of Northern and Mediterranean air masses. At the sub-daily time step, the d_v-q correlation observed during the q-increase period of the day results from the addition of local evaporation. We have proposed a depiction of typical daily cycles of water vapor isotopic composition under different meteorological conditions, which could be used as a framework for further quantitative analysis of vapor sources during specific periods.

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Table 1. Isotopic compositions of laboratory standards (δ_{LS}), and statistics on raw measurements from all calibrations (average and standard deviation of δ_{raw} from 40 data between 20 July to 24 August 2011).

		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

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

	$\delta^{18}O$	δD
	Water vapor concentration	
Slope	$-0.16\ 10^{-4} \pm 0.13\ 10^{-4}$	$6.08\ 10^{-4} \pm 0.99\ 10^{-4}$
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

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

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

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

	$\delta^{18}O$ (‰)		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 ($mmol.mol^{-1}$)	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

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

	North Atlantic [310°-360°]	Mediterranean [110°-220°]	Bay of Biscay [220°-310°]
N	10	13	13
$\delta^{18}O$ (‰)	-15.83	-13.13	-14.90
δD (‰)	-103.5	-86.5	-96.3
d_v (‰)	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

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

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

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

Figure 4. Hourly day-time and night-time isotopic composition of atmospheric water vapor in according to air mass origin. For reference, the GMWL and LMWL are also plotted.

Figure 5. 24-hour average values of $\delta^{18}O$, δD, deuterium excess (d), relative humidity (RH), mixing ratio (q) and planetary boundary layer height (PBLH) calculated from 20 July to 24 August 2011 according to air mass origin. Grey shading indicates standard deviation of each average.

Figure 6. Relationships between 24-hour average values of δ_v and 1/q according to the two main air mass origins, and corresponding linear regressions for the period of q increase (see text). Squares indicate the isotopic composition of the local vapor end-member calculated for a mixing ratio corresponding to saturation at the water surface temperature.

Figure 7. 24-hour average values of δ_v according to the two main air mass origins, corresponding linear regressions for the period of q increase (see text), and calculated local vapor end-member (see Figure 6 for details). For reference, the LMWL is also plotted.