

We would like to thank the reviewer for taking the time to read our manuscript and giving detailed feedback, which helped us to improve the manuscript. Please find our answers to the comments (*in italics*) in the following. Citations from the paper are marked **in blue**, and **blue bold** refers to text added/changed in the revised manuscript.

1 Major comment: molecular diffusion in the boundary layer is not significant beyond the first centimeters above the surface

Kinetic fractionation can happen because different isotopologues have different molecular diffusivities (Merlivat (1978); Merlivat and Jouzel (1979); Jouzel and Merlivat (1984)). This plays a role only where molecular diffusion is significant. In the planetary boundary layer, molecular diffusion plays a significant role only in the first millimeters above the surface (Holton (1973); Stull (1988)). Beyond the first centimeters, it can be completely neglected and turbulence is the main factor (see for example fig 7.1 in Stull (1988)). This is a well-established property of the boundary layer. No isotopic fractionation is associated with turbulence. Therefore, molecular diffusion and associated isotopic fractionation cannot explain the vertical gradients in isotopic composition observed at the scale of several meters.

The reviewer is correct; non-equilibrium fractionation during ocean evaporation due to diffusion mainly occurs in the first centimeters above the ocean surface. Even though non-equilibrium fractionation is not expected to occur at several meters height above the sea surface, it still affects the isotopic composition of water vapour at higher levels through transport processes and due to turbulent mixing that mixes the freshly evaporated water vapour with water vapour at higher levels. Thus, the *effect* of non-equilibrium fractionation also impacts the vertical isotope profiles in the whole boundary layer.

Although we do see a stronger influence of non-equilibrium fractionation on the vertical isotope profile at low wind speeds (as shown in detail in our reply to referee 2), we agree that the influence of non-equilibrium fractionation alone cannot explain the observed vertical gradient. Therefore, we will not discuss the effects of non-equilibrium fractionation and its influence on the vertical SWI gradients in this study, and we deleted the non-equilibrium fractionation from the framework explaining the observed vertical profiles (see also our response to the following comments).

The authors cite Tanny and Cohen (2008) to justify the existence of diffusion processes and associated isotopic fractionation in the turbulent part of the boundary layer. This article is mis-interpreted and mis-used here. Tanny and Cohen (2008) argues that some coherent structures, and not just random eddies, are responsible for the transport in the first centimeters above the surface. This has implications for how we calculate the evaporation flux and its composition (Craig and Gordon (1965) equation). But this article never refutes the well-established property that turbulence dominates beyond the first centimeters above the surface, and never argues that we should modify how we interpret the vertical gradients of constituents at the scale of several meters. In fact, the processes discussed in Tanny and Cohen (2008) are so close to the surface that they are all supposed to be encapsulated in the evaporation flux equation and in the Craig and Gordon (1965) equation.

Thank you for this comment. We removed the reference to Tanny and Cohen (2008), which was indeed misleading in the context of the interpretation of the vertical profiles over 13 m above the ocean surface.

The decrease of δD and $\delta^{18}O$ with height, at scales of several meters or larger, has already widely been documented in observations (e.g. Ehhalt (1974); Bailey et al. (2013); Sodemann et al. (2017); Salmon et al. (2019)). There is a simple reason for this negative vertical gradient. In the free troposphere, condensation depletes the water vapor. In the boundary layer, all the vapor ultimately comes from the mixing between freshly evaporated water vapor (enriched), and vapor from the free troposphere that has already undergone condensation (depleted). The proportion of freshly evaporated water vapor decreases with height. This is why δD and $\delta^{18}O$ decrease with height in the boundary layer. The fact that numerical models at various resolutions (general circulation models, large-eddy simulations...) can reproduce the negative vertical gradient without representing molecular diffusion within the boundary layer is an additional proof that no molecular diffusion needs to be involved to explain this feature. The same rationale can apply for d-excess. At the scale of the troposphere, observations suggest that free tropospheric vapor that has undergone significant distillation has a high d-excess (Sayres et al. (2010); Samuels-Crow et al. (2014)). Numerical models at various resolutions can reproduce this increase in d-excess with altitude through the troposphere without representing molecular diffusion within the boundary layer (Bony et al. (2008); Blossey et al. (2010)). Again, this is an additional proof that we can explain an increase in d-excess with altitude without involving molecular diffusion. At the scale of the boundary layer, vertical profiles can be more diverse (e.g. Sodemann et al. (2017); Salmon et al. (2019)), maybe due to the non-monotonic evolution along the distillation and to the stronger effect of droplet or rain evaporation (Salmon et al. (2019)). But in the case where d-excess in the free troposphere or in the upper part of the boundary layer is high, following the same rationale as for $\delta^{18}O$ and δD , we expect d-excess to increase with height in the boundary layer.

Thank you for pointing this out. We agree that diffusive processes are not needed to explain the observed vertical SWI gradients. Therefore, we do not use this process to explain the vertical SWI gradients in this study anymore. We explain the changes made to the manuscript in the following, point by point:

As a consequence, several sentences need to be modified:

- a) p 215: “and dominating effect from non-equilibrium fractionation” needs to be removed. Non-equilibrium fractionation where? In the atmosphere or at the surface? If you mean in the atmosphere, it’s wrong as explained above. If you mean at the surface, it’s probably wrong as well, because weak vertical turbulent mixing is probably associated with higher relative humidity at the surface and thus weaker kinetic fractionation.

We removed this part of the sentence.

We would still like to mention in this reply, that non-equilibrium fractionation at the ocean surface can influence the isotopic composition of the MBL by upward turbulent mixing. During ACE, we encountered low wind speeds at high and low relative humidity (see figure A). Weak turbulent mixing can also occur together with low relative humidity and, thus, can also be associated with substantial non-equilibrium fractionation (see blue points at low RH_{SST} in Fig. A).

We changed the text as follows:

“Using sea spray concentrations and sea state conditions, we show that the vertical SWI gradients are particularly large during high wind speed conditions with increased contribution of sea spray evaporation or during low wind speed conditions due to weak vertical turbulent mixing *and dominating effect from non-equilibrium fractionation.*”

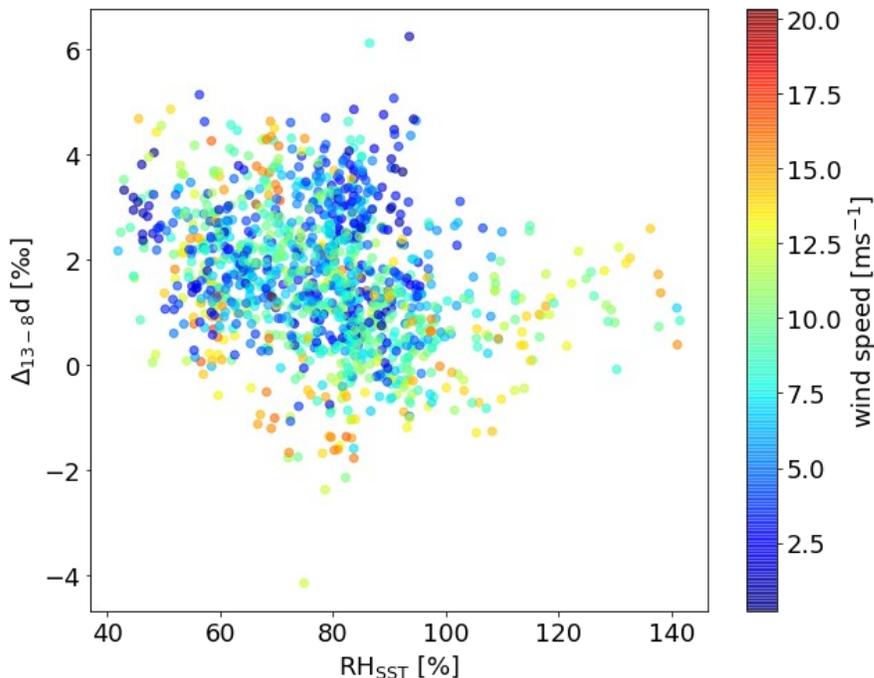


Figure A: Scatter plot of ACE measurements showing relative humidity with respect to sea surface temperature [RH_{SST}] versus the vertical difference in d-excess [$\Delta_{13-8} d$] coloured by wind speed measured at 30 m above the ocean surface.

b) p 3 l 31- p 4 l 4: to be removed, because Tanny and Cohen (2008) is mis-interpreted here.

Removed as suggested.

c) p 16 l 21-22: to be removed.

Removed as suggested.

d) p 17 l 27-30: this hypothetically turbulence-free atmosphere is too unrealistic to be used as a started point for interpreting vertical gradients at the scale of several meters. Non-equilibrium fractionation only impacts the composition of the evaporation flux, not the vertical gradients. The 1st process may thus be either removed, or replaced by the fact that the isotopic composition of the evaporation flux is more enriched and has a lower d-excess than the water vapor that has already undergone distillation.

We removed the first process and changed the text to:

“Two main processes are taken into account in this framework: (1) vertical turbulent mixing, which increases with wind speed, leads to a well-mixed atmospheric layer close to the ocean surface and, thus, weakens the vertical SWI gradients; and (2) the sea state

determines the production of sea spray and the influence of sea spray evaporation on SWI composition. The proposed framework considers the three wind regimes introduced in section 4.2.1, in which these two processes are expected to differ in strength. As a consequence, vertical turbulent mixing and sea spray evaporation exert a varying influence on the vertical SWI gradient in the lowermost MBL.”

- e) p 18 l 2-4: remove “Due to moisture ... weak turbulence”. The previous sentence is a sufficient explanation and can be replaced by: “This leads to ... with strong vertical moisture and isotopic gradients”.

We changed the text as follows:

“First, for low wind speed conditions with high wave age in regime I (Fig. 12a), weak vertical turbulent moisture transport is expected. **If the MBL vertical moisture gradient results from linear mixing of freshly evaporated water vapour from the ocean surface with moisture from the free troposphere, which likely experienced condensation previously, then lower layers are expected to have higher δ -values than upper layers. In such a scenario, weak vertical mixing leads to strong vertical gradients of specific humidity and δ -values. Non-equilibrium fractionation at the ocean surface during evaporation strongly impacts d in the ocean evaporation flux. Therefore, the vertical d -gradient in the lower MBL depends on the strength of non-equilibrium fractionation at the ocean surface. If we assume a simple “two end-member”-mixing process in the MBL of freshly evaporated water vapour with free tropospheric air masses that have undergone substantial rainout, the vertical gradient in d is defined by the difference in d between these two end-members. Free tropospheric air masses, which have lost a major fraction of their water vapour during rainout, show a d in water vapour which closely follows a Rayleigh distillation process (Samuels-Crow et al., 2014) and are expected to have high d by the definition of d (see e.g. Dütsch et al., 2017). d in freshly evaporated water vapour is therefore expected to remain below d of free tropospheric air masses that have undergone substantial rainout previously. An effect by sea spray evaporation is not expected in this wind regime as only little sea spray is produced at low wind speeds. This simple interpretation framework could explain the observed conditions with enhanced gradients in $\delta^{18}\text{O}$, $\delta^2\text{H}$ and d at low wind speeds (regime I) compared to medium wind speeds (regime II). However, recent studies (e.g. Sodemann et al., 2017 and Salmon et al., 2019) showed that the vertical gradients in particular of d rarely follow a simple two end-member mixing model. Differential transport processes in the boundary layer as well as convective plumes with enriched water vapour (and lower d) are probably responsible for the large variability in the observed vertical isotope profiles. Therefore, further analysis, which goes beyond the scope of this study, is needed to quantify the wind dependency of non-equilibrium fractionation and its effect on the vertical d gradient in the MBL.”**

- f) p 18 l 7: remove “weakens ... by diffusion”

Removed as suggested.

- g) p 19 l 23: remove “vertical moisture diffusion, ”

Removed as suggested.

h) p 19 l 26: remove “*The effect ... such situations*”.

Removed as suggested.

2 Minor comments

- a) p1 l 16: “moisture loss during transport”: if moisture loss happens in clouds, it does not directly impact the isotopic composition of the vapor near the surface. Replace by something like: “mixing with air masses that have lost moisture during their transport”?

We analysed backward trajectories computed from a vertical stack of starting points within the boundary layer above the ship’s position. Figure B illustrates that the changes in specific humidity, on which the moisture loss to source ratio is based, also occur in the air masses arriving close to the ocean surface. There are increases as well as decreases in specific humidity along these trajectories, and the decreases in specific humidity can occur close to the arrival time and mostly during the ascent of air masses which generally means that cloud formation and precipitation changes the isotopic composition of the air masses directly.

Therefore, we do not change this sentence.

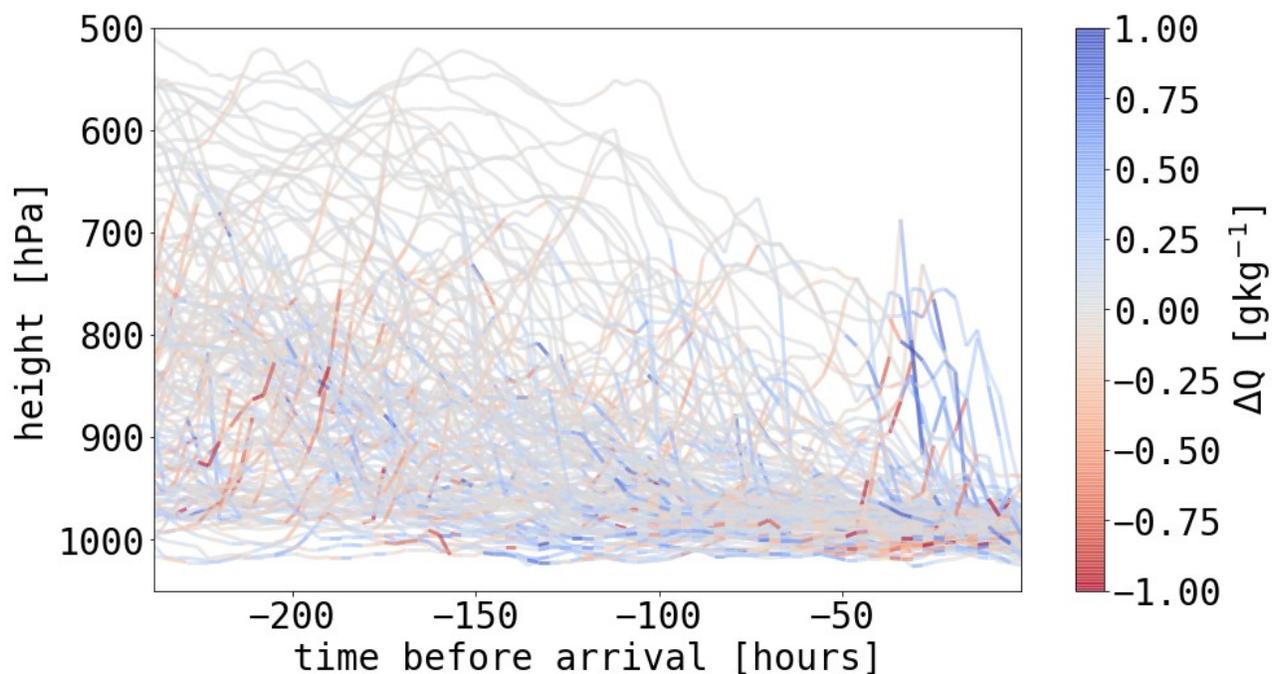


Figure B: 10-day backwards trajectories from legs 1-3 starting between 0 and 40 hPa above sea level pressure. Colours denote changes in specific humidity between two consecutive time steps (positive value denotes increase in specific humidity).

- b) p1 l 18: “low” -> “weak”.

Changed as suggested:

“In the subtropics and tropics, persistent anticyclones lead to well-confined narrow easterly moisture source regions, which is reflected in the **weak** SWI variability in these regions.”

- c) p1 l 19: ”at different heights”: this misleads the reader to think there are many heights -> specify “at 8m and 13m”.

Changed as suggested:

“Furthermore, the ACE SWI time series recorded at 8 m and 13 m above the ocean surface provide estimates of vertical SWI gradients in the lowermost marine boundary layer.”

- d) p2 l 12-13: *These citations are not very relevant here. Cite papers that really show the point. These cited papers just look at the effect of atmospheric processes on the isotopic composition, but we knew about these atmospheric processes long before 2018. These papers can be usefully cited elsewhere.*

Replaced by:

“The main source for atmospheric water in oceanic regions is ocean evaporation which is strongly influenced by the large-scale atmospheric flow (Simmond and King 2004, Papritz et al., 2014) as well as small-scale turbulent and convective mixing (Jabouille et al. 1995, Sherwood et al. 2010).”

- e) p3 l 8: *“MBL moisture budget”: we do not need isotopes for this -> “MBL isotopic budget”*

Unchanged: SWI help to pinpoint the influence of different moist processes such as sea spray evaporation or below-cloud effects (e.g. precipitation evaporation), which are difficult to identify without the use SWI (e.g. Aemisegger et al., 2015; this study)

- f) p3 l 30: *how do you define the top of the MBL here? Is it the cloud top or cloud base?*

For the three-layer model, we define the MBL top as the cloud base because cloud processes are not included in this simplified model of MBL processes.

- g) p 4 l 8: *here a bit more background would be necessary to understand what is the wave age. Is it related to a time unit, e.g. seconds or minutes or hours? What does it physically mean when it is <1?*

The text was changed to:

“The sea state can be described by the dimensionless wave age, which is the ratio of the phase speed of the dominant wave component of the sea state to wind speed (Young, 1999). The wave age describes the ability of waves to absorb energy from the wind and hence represents stages of their development process. On the one hand, when waves are young (wave age $\sim <1.0$), waves travel slower than wind and thus are strongly forced by the atmosphere. As a result, waves absorb energy from the wind, grow rapidly and eventually break, generating sea spray (see e.g. Toffoli et al., 2017). When the sea state is mature (wave age >1.0), on the other hand, waves travel faster than the wind and no longer absorb energy from it. Under these circumstances, waves are independent from the wind and assume a gently sloping profile, which makes them less prone to breaking and spray generation.”

- h) p11 l 24: *“to assess moisture sources”: we do not need SWI for this -> “to assess the effect on SWI of moisture sources”*

We changed the text as suggested:

“The five-month time series of SWIs in water vapour provide the unique opportunity to assess **the effect** of moisture source and transport processes **on SWIs** in the MBL on various time scales and under diverse climatic conditions.”

i) p 14 l 21: “not shown”: it would be useful to add this plot in the main text or in SI.

The meridional variability in source latitude is already shown indirectly in Fig. 8. As shown in the figure below, there is an increase in the standard deviation of the weighted mean moisture source latitude ($lat_{ms,sd}$, blue line) in the extratropics compared to the tropics, except for the bin between 0 and 10°N. The ITCZ lies within this bin, with moisture source locations either north or south of the ITCZ. This induces a large $lat_{ms,sd}$. To keep the paper concise and limit the number of figures, we don't show it in the paper, but add it to the supplementary material.

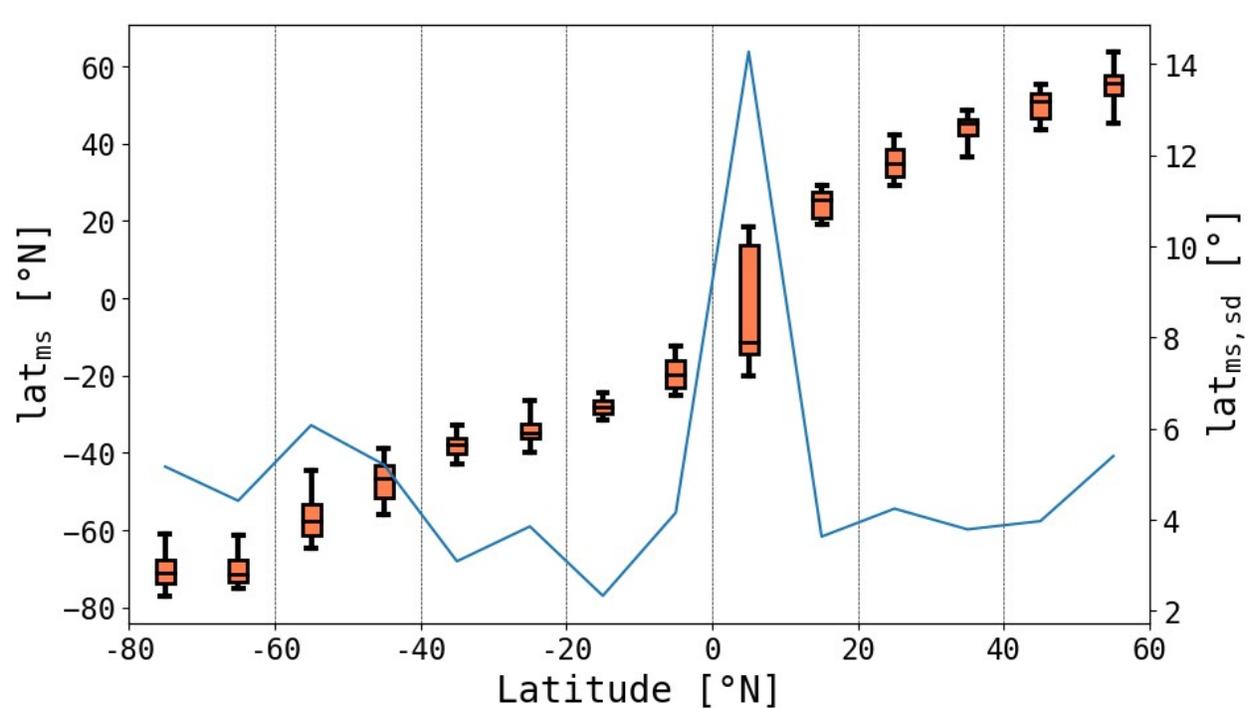


Figure C: Box plots of meridional variations in the weighted mean moisture source latitude for all legs showing mean (black horizontal line in box), interquartile range (orange boxes) and [5,95]-percentile range (whiskers) in bins of 10° latitudinal width. The blue line shows the standard deviation of the weighted mean moisture source latitudes of each 10°-bin.

j) p15 l 5: remove “(Fig 8)” which does not show the point.

Removed as suggested.

k) p 15 l 20: “larger degree of precipitation” -> “larger variability in the precipitation”: here you want to explain the isotopic variability, not its mean value.

Changed as suggested:

“... but also due to **larger variability in the** precipitation along these pathways.”

- l) p 18 l 17-19: to verify these mechanisms, observations won't be sufficient. Large-eddy simulations would be useful. A sentence to mention this could be added.

Added as suggested:

“Furthermore, modelling of the isotopic composition in the MBL with various approaches spanning from simple mixing models to large-eddy simulations could help to understand the measured profiles.”

- m) p 19 l 9: “more important” -> “more variable” (same comment as p 15 l 20)

Changed as suggested:

“Furthermore, moisture loss during transport, which affects the SWI composition of water vapour, is more **variable** in the extratropics than in subtropical and tropical regions.”

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