Authors' reply to comment on *Meridional and vertical variations of the water vapour isotopic composition in the marine boundary layer over the Atlantic and Southern Ocean* by Anonymous Referee #2

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 comments

1. Uncertainty evaluation: The second message of the manuscript (section 4.2) details the vertical differences between two infrared spectrometers that were installed at 8 and 13 meters, respectively. On average, significant differences are observed between these two instruments. A significant amount of work is dedicated in this manuscript into characterising the instruments performances. Yet, the results in section 4.2 do not include an error bar for which the differences are significant between the two instruments. In particular, in Fig. 10, a significant number of datapoints presented have very small difference (< 0.2 ‰ in δ18O for instance). Considering the precisions of the instruments (in particular the 2120), it is difficult to assess the relevance of these datapoints. This is a key aspect to be able to justify the wind speed dependency, and it seems that most of the results necessary to evaluate the statistical significance of the results are already presented here. I would suggest make use of the standard deviation of the differences (for instance in Fig. 5) and use pertinent statistical tests (for instance Kruskall Wallis tests) to evaluate in which cases are the differences statistically significant.

Thank you for pointing this out. We included the uncertainty introduced by the post-processing of the SWI measurements in Fig. 10, which shows that the standard deviation of the vertical differences in each bin is larger than the uncertainty due to the post-processing.
Furthermore, we conducted a Kruskall Wallis test for the three wind regimes to test for statistically significant differences in the vertical SWI gradients of the three regimes. The three groups differ significantly for $\delta^{18}O$, $\delta^{2}H$ and *d* according to the Kruskall Wallis test (*p*-value on the order of 10^{-12}). As highlighted by Nicholls (2001), the interpretation of null-hypothesis significance tests needs to be done carefully as the sample size strongly influences the outcome of such tests with a higher probability for rejecting the null hypothesis with increasing sample size. Therefore, we prefer to discuss the confidence intervals (instead of the significance test) in this study.

2. In the manuscript, the authors do not provide any quantitative evaluation of the vertical differences of the isotopic composition in the marine boundary layer. Yet, formulations have been predicted, based on very limited number of observations compared to this study. While I generally agree with the qualitative proposition of the authors, I believe that they should have tested previous formulations. From articles already mentioned in the manuscript, I would suggest to compare their results to models of isotopes in the boundary layers, namely Craig (1965), Merlivat (1978), or again Benetti et al. (2018). I would suggest to use formulations developed in Cappa et al. (2003), and the parametrisations of Merlivat (1978) for the dependency of the diffusion with turbulence. I suggest that these parametrisations, which already include an increasing impact of turbulence with wind speed, should be tested. Due to the considerable amount of data of the authors, I would suggest evaluating this on typical cases (for instance, the regimes [I], [II] and [III] identified by the authors. Also, as here δ18O is expected to decrease monotonously with height, I would suggest that the authors identify the different contributions to d-exc and δ18O (or δD and δ18O) in an isotope-isotope space (for instance *δD vs δ18O) and illustrate which process is characterized with slopes higher or lower than the meteoric water line.*

Thank you for this proposition. Our response to this comment addresses three points brought up by the reviewer:

1) **Application of existing models such as Craig and Gordon (1965), Merlivat (1978) or Benetti et al. (2018):**
   As suggested, we tested previous formulations of isotopic models for the marine boundary layer such as for example the combined evaporation-vertical mixing model by Benetti et al. (2018) to predict the SWI composition at 8 m a.s.l from the SWI measurements at 13 m. The SWI-13 measurements provide the isotopic composition of the air parcels mixed in from above and the ocean evaporation flux is defined by the Craig-Gordon model (see Benetti et al. 2018 for more details). However, because we do not have calibrated specific humidity data for SWI-8, we have to estimate the fraction of water vapour that is mixed downward based on an estimated specific humidity profile. Note that due to logistic reasons, it is not possible to calibrate the SWI-8 measurements a posteriori. Our results from applying the Benetti et al. model in this setup shows that the predicted isotope time series for SWI-8 strongly depends on the chosen value of the specific humidity at 8 m a.s.l. Furthermore, we think that the large variety of vertical SWI profiles measured in this study and in more detailed aircraft-based studies such as Sodemann et al. (2017) and Salmon et al. (2019) show that the processes involved in shaping these vertical profiles are likely more complex. In particular, we think that horizontal advection and the formation of convective plumes can lead to a variety of profiles that cannot be predicted without a 3D numerical model (isotope-enabled LES or high resolution regional numerical weather prediction model). We therefore do not find it straightforward to use existing simple models to predict the vertical gradients within the marine boundary layer. Please also note that detailed simulations with the isotope-enabled model COSMOiso have been performed around Antarctica and will be compared to the ACE measurement data in a follow-up study.

2) **The use of the formulations developed in Cappa et al. (2003), and the parametrisations of Merlivat (1978) for the dependency of the diffusion on turbulence:**
   A closer investigation of the dependence of the non-equilibrium fractionation factor on diffusion and turbulence within the three regimes presented in the manuscript based on the ACE data is an excellent idea. We thank the reviewer for this suggestion.

   We used the non-equilibrium fractionation factor as described by Cappa et al. (2003) to calculate the relative importance of turbulent and diffusive transport. In their equation 5, Cappa et al. (2003) described the non-equilibrium fractionation factor as the ratio of the molecular diffusivity of the heavy isotope (D_H) and the light isotope (D_L) to the power of n. Here we use the diffusivity ratios from Merlivat (1978).

$$\alpha^*_{\text{diffusion}} \frac{K_H}{K_L} = \left[\frac{D_H}{D_L}\right]^n,$$

   Equation 5 from Cappa et al. (2003).

The exponent *n* is equal to zero if the transport during ocean evaporation is completely turbulent (i.e. if no non-equilibrium fractionation occurs), and equal to 1 if the transport is completely diffusive. Therefore, if *n* increases, non-equilibrium fractionation becomes more important. One way to estimate *n* from point measurements is to use an existing relation between the *d*- h_s slope, where h_s is the relative humidity with respect to the sea surface temperature, and the exponent *n* that is based on the linearised Craig Gordon model and the closure assumption (see Aemisegger and Sjolte 2018 for more details). In a purely turbulent regime, in which no non-equilibrium fractionation occurs, *d* is insensitive to changes in h_s and therefore the *d*- h_s slope is 0. In the case of a purely diffusive regime, *d* is very sensitive to *h* and therefore the *d*- h_s slope is steep. The following expression can be found using the linearized Craig Gordon model linking the *d*- h_s slope and the exponent *n* (see Aemisegger and Sjolte 2018 for more details): $n = -0.53045 * s_{d(hs)} - 0.00699$, where $s_{d(hs)}$ is the slope of the linear relation between *d* and h_s. We calculated $s_{d(hs)}$ for legs 1-3 using the 1-hourly measurement points within 3-day running windows using the measurements at 13 m.

As expected and shown in Fig. A, *n* increases with decreasing wind speed. During periods with large differences in $\delta^{18}O$ and *d* between the two measurement heights, high values of *n* are often observed. The mean *n* over all legs is 0.128±0.070, which lies below the values (0.22 – 0.25) found by other studies (Gat et al., 1996; Pfahl and Wernli, 2008). The reason for the low *n* in this study is the flatter *d*-h_s slope of –0.38‰/% (for RHsst<1.0, when ocean evaporation can occur) compared to slopes between –0.57‰/% and –0.42‰/% from previous studies using measurements (Steen-Larsen et al., 2014, 2015; Benetti et al., 2015; Uemura, 2008). A slope of –0.38‰/% however lies within the range of values obtained for the Southern Ocean by Aemisegger and Sjolte (2018) using the closure assumption and the Craig Gordon model based on ERAinterim reanalysis data (compare their Fig. 9b).

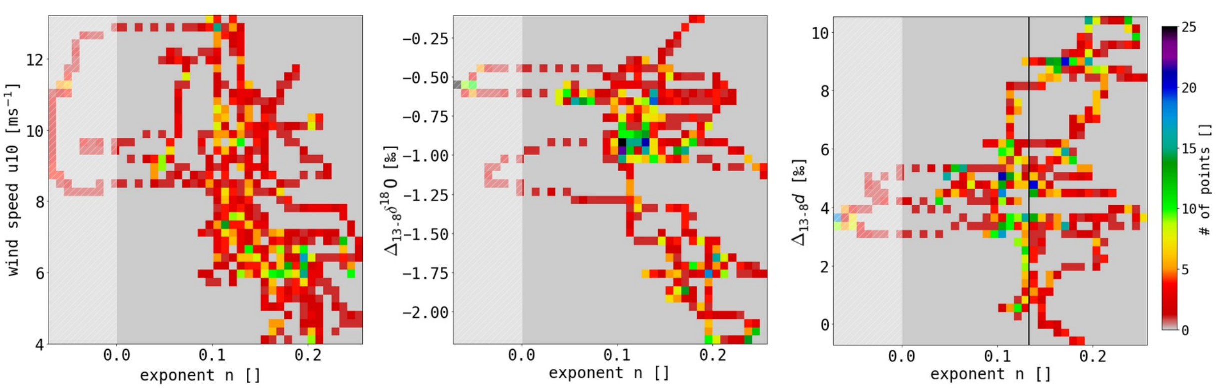

Figure A: Bi-dimensional histograms of n versus wind speed (left), $\Delta_{13\text{-}8}\delta^{18}O$ (middle) and $\Delta_{13\text{-}8}d$ (right), coloured by number of points per bin. n is calculated using all 1-hourly measurement points of h_s and d within a 3-day moving window and the linearised Craig and Gordon model (Aemisegger and Sjolte 2018). The vertical black line denotes the mean value of n over all legs of 0.128. Wind speed, $\delta^{18}O$ and d are 72-hour moving averages. Values of n<0 are overlaid by white hatches. Note that for these measurement periods h_s was larger than 1.0 indicating dew deposition, in which the above framework for evaporative conditions is not valid.

3) **Analysis of three regimes in the δD-δ^{18}O phase space and comparison to the meteoric water line.**

We compared the three wind regimes in terms of their behaviour of the isotope measurements in the δ^{18}O- δ^{2}H-space (Fig. B). Due to the low SST for a large part of the ACE track for legs 1-3, *d* is lower than 10 for most of the measurement points. Therefore, these points are below the meteoric water line. For regime I, most of the points are below the meteoric water line. For regime II and III, 12% of all points, most of which with high δ-values, are above the meteoric waterline.

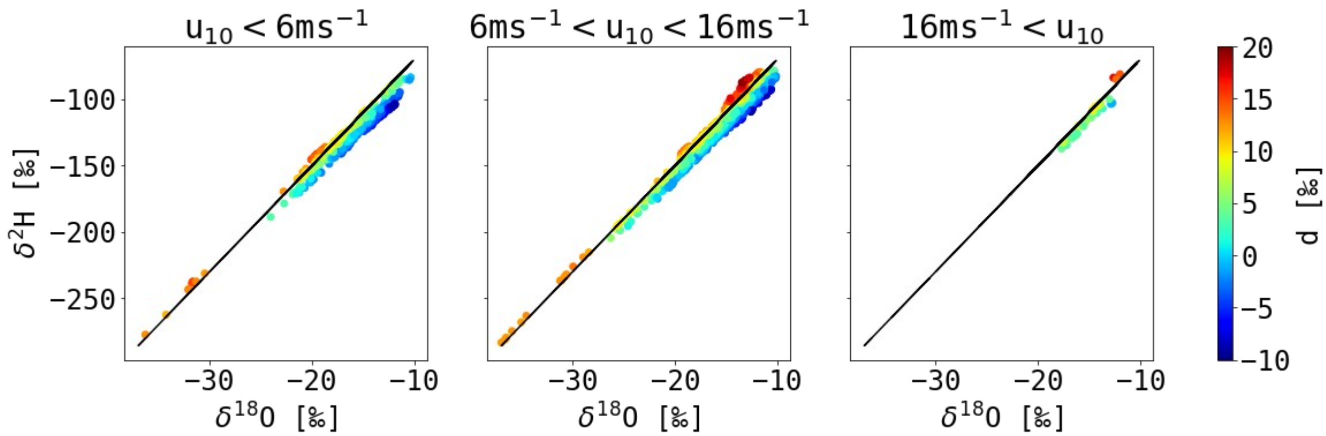

Figure B: Scatterplots of δ^{18}O versus δ^{2}H, coloured by d, for the three wind regimes using 1-hourly SWI-13 measurements from legs 1-3. The black line shows the meteoric water line ($\delta^{2}H = \delta^{18}O*8+10$)

Because this analysis goes beyond the scope of this study, and to keep the manuscript concise as the editor requested when we submitted the manuscript, we decided not to include these results. Furthermore, we think that the qualitative discussion in the paper is adequate given the unfortunately missing vertical profiles of specific humidity. We agree that a study that investigates the factors influencing the exponent *n* in different synoptic situations and on the relative importance of turbulent and diffusive transport near the ocean surface would be a very useful follow-up of the present study. The (open-access) data set provides many opportunities for additional investigations including a comparison study of different MBL isotope models.

Changes to the manuscript:

- We now mention the idea on an evaluation of various MBL mixing models and a closer analysis of the influence of diffusion during ocean evaporation in future studies with the ACE datasets:

  ”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.”

2 Minor comments

a) *Page 2, Line 10: "The atmospheric water cycle is an essential component of the Earth's climate system" The water cycle is not just atmospheric by definition.*

Changed to: "The atmospheric **branch of the** water cycle is..."

b) *Page 2, line 24:*
"SWIs are tracers of moist atmospheric processes because they record phase changes in the atmosphere." What is a moist atmospheric process ? Sentence unclear

Changed to: "…SWIs are tracers of **atmospheric processes involving phase changes of water.**"

c) *Page 3, line 28 to 35: I would suggest include articles such as (Craig, 1965; Cappa et al., 2003).*

We added two sentences (pages 3/4) on the modelling of SWIs in the MBL during evporative conditions referring to previous studies:

"A similar view of the lower MBL, dividing it into a thin laminar layer close to the ocean surface and a turbulent layer above, was used by Craig and Gordon (1965) to calculate the isotopic composition of the evaporative flux from the ocean surface. The Craig-Gordon (1965) model has been applied and refined in various studies and has been shown to adequately simulate the isotopic composition of the MBL water vapour under evaporative conditions (e.g. Merlivat and Jouzel, 1979; Gat, 2008; Horita et al., 2008; Pfahl and Wernli, 2009; Benetti et al., 2018; Feng et al., 2019)."

d) *Page 4, line 5 to 19: The link with the isotopes and their limits in this context is missing.*

We added a sentence about why we are interested in turbulence in MBL/close to ocean surface:
"Ship-based measurements are normally situated in the surface layer of the MBL and thus directly influenced by turbulent conditions."

e) We added a sentence addressing the limitation of using isotopes to analyse sea spray evaporation:
It is difficult to directly measure sea spray evaporation and, therefore, it is still an open question to what extent sea spray evaporation affects moisture in the MBL (Veron et al., 2015) in different wind forcing conditions.

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