Atmospheric
Chemistry
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Discussions

Interactive comment on "Meridional and vertical variations of the water vapour isotopic composition in the marine boundary layer over the Atlantic and Southern Ocean" *by* Iris Thurnherr et al.

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This article presents new isotopic measurements during a cruise in the Atlantic Ocean. This cruise has the advantage of spanning a wide latitudinal range. This paper thus contributes to a better description of the latitudinal distribution of isotopic variables and of its variability. Another significant contribution of this paper is to document the isotopic composition at two different altitudes, thus giving some idea of the vertical gradient in the lower part of the boundary layer.

The paper is well written and the figures are of good quality. The measurement methods and possible errors are explained in detail.

In addition to a few minor comments, I have one major comment: I think that the interpretation of the vertical isotopic gradient is faulted because a well-established property of the boundary layer is ignored: molecular diffusion in the boundary layer is not significant beyond the first centimeters above the surface. Fortunately, this fault does not affect the main conclusions of the paper and can be easily corrected.

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 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.

The decrease of δD and $\delta^{18}O$ with height, at scales of several 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.

As a consequence, several sentences need to be modified:

- p 2 l 5: "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.

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

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

- 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.

- 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".

- p 18 l 7: remove "weakens ... by diffusion"

- p 19 l 23: remove "vertical moisture diffusion, "

- p 19 l 26: remove "The effect ... such situations".

2 Minor comments

- p 1 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"?

- p 1 l 18: "low" -> "weak".

- p 1 l 19: "at different heights": this misleads the reader to think there are many heights -> specify "at 8m and 13m".

- p 2 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.

- p3 l 8: "MBL moisture budget": we do not need isotopes for this -> "MBL isotopic budget"

- p 3 l 30: how do you define the top of the MBL here? Is it the cloud top or cloud base?

- 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?

- p11 l 24: "to assess moisture sources": we do not need SWI for this -> "to assess the effect on SWI of moisture sources"

C5

- p 14 l 21: "not shown": it would be useful to add this plot in the main text or in SI.

- p 15 l 5: remove "(Fig 8)" which does not show the point.

- 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.

- 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.

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

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