

Review RC2 - acp-2022-12

Thurnherr and Aemisegger provide a detailed, well-written manuscript that seeks to investigate the process-level causes of low vapor d-excess observed during the 2016/17 Antarctic Circumnavigation Expedition. They apply three single-process models representing impacts on isotope ratios from (a) ocean evaporation, (b) dew formation and deposition, and (c) upwind distillation, and demonstrate that these three processes follow diagnostic pathways in d_{18O}/d -excess space. They then also compare the results from their process models to a regional NWP model simulation including isotopes to validate these models. Taken together, they suggest a larger than previously appreciated role for dew formation over the ocean for altering the d-excess of near-surface water vapor, particularly in the warm sector of extratropical cyclones.

Their analysis is rather detailed, and the process modeling provides interesting insights into the evolution of d-excess in near-surface water vapor. This paper represents a nice contribution, and only have a handful of suggestions for revision below.

Reply: We thank the reviewer for their positive feedback, and their comments, which helped to improve the clarity of the manuscript.

Line-by-line notes

1. L. 36 - there appears to be an extra '2' in the denominator for R here.

Reply (as for Reviewer 1, comment 1): The 2RVSMOW2 atomic isotope ratio is multiplied by 2 because of the two possible positions of the deuterium in the water molecule (see equivalence of atomic vs. molecular ratios in Kerstel, 2004 and Iannone et al. 2010). To avoid confusion we now use the molecular isotope ratio for the standard and write $2RVSMOW2=3.1152\cdot 10^{-4}$, while removing the multiplication by 2 in the definition of δ^2H . The text was adapted accordingly.

2. L. 44-46: might be good to cite a few of the observational studies that dew formation is a non-equilibrium process (e.g., Deshpande et al., 2013; Wen et al., 2012), since condensation processes are still (often) thought of as equilibrium to first order.

Reply: Thank you for this suggestion. We added a few references to observational studies of dew formation and mentioned that this topic has been addressed more specifically in studies over land. We changed the text as follows:

"For example, humid air that is supersaturated with respect to the sea surface temperature (SST) can experience dew deposition on the ocean surface, which is

accompanied by non-equilibrium fractionation due to the humidity gradient towards the ocean surface (Thurnherr et al., 2021). Dew deposition and the non-equilibrium fractionation effects accompanying it has been extensively studied over land as a water input into different ecosystems (e.g., Wen et al., 2012; Li et al., 2021).”

3. L. 61-62: d can also change purely due to equilibrium effects when the Rayleigh f is very low (e.g., Bony et al., 2008; Dütsch et al., 2017)

Reply: We adjusted the sentence to include this. Actually, as we showed in Appendix A of Thurnherr et al. (2021), d can also be altered at higher f due to the temperature dependency of equilibrium fractionation. We therefore adapted the text as follows:

“During this long-range transport, d can change due to non-equilibrium processes or changes in the ambient temperature that impact the ratio of the equilibrium fractionation factors of $^1\text{H}_2^{18}\text{O}$ and $^1\text{H}^2\text{HO}$ (Dütsch et al., 2019, Appendix A in Thurnherr et al. 2021).”

4. L. 104: which laser spectrometer was used and how was it calibrated?

Reply: We used a Picarro cavity ring-down laser spectrometer. The instrument and measurements are characterised in detail in previous studies (Aemisegger et al. 2012, Thurnherr et al. 2020). To keep this manuscript concise, we’d like to keep this section as short as possible. We changed the text as follows (at L. 111):

“For the isotope measurements a Picarro cavity ring-down laser spectrometer was used. The instrument and measurements are characterised in detail in previous studies (Aemisegger et al., 2012; Thurnherr et al., 2020).”

5. L. 115: could the authors clarify what explicit treatment of deep convection means (i.e., is this model non-hydrostatic)?

Reply: Yes, COSMO_{iso} is a non-hydrostatic model and we switched off all convection parametrisations (deep, mid-level and shallow convection). To explain more explicitly why we switched off all convection parametrisations, we adapted the text as follows at L. 113:

“The limited-area model COSMO_{iso} (Pfahl et al. 2012) is an isotope-enabled version of the non-hydrostatic numerical weather and climate prediction model COSMO (Steppeler et al., 2003). The one-month, nudged COSMO_{iso} simulation was performed for the time period 13 Dec 2016 to 12 Jan 2017 with a horizontal grid spacing of 0.125° , corresponding to ~ 14 km, 40 vertical levels and treating deep convection explicitly (shallow and deep convection parametrisations were switched off). The choice of treating convection explicitly at the resolution of the model grid is motivated by insights from recent studies (e.g. Vergara-Temprado et al. 2020), which show that convection parameterization schemes can be switched

off at coarser resolutions than previously thought (e.g. on the order of 10 km). Such a setup with explicit convection has been evaluated carefully by comparing it to COSMO_{iso} simulations with parametrised convection and isotope observations from multiple platforms in previous studies (Dahinden et al. 2021, de Vries et al. 2022). The chosen grid spacing of 14 km allows for a large domain spanning an area of 50°x50° that is centred at 47°S, 18°E (Fig. 1a) and within which the regional model can develop its own isotope meteorology at the mesoscale, which is independent of the global model driving the COSMO_{iso} simulation at the boundaries.”

6. L. 136-137: These seem to be fairly unusual choices for the isotope ratio of the ocean, could the authors clarify how these values were chosen? This is of particular note for this manuscript as it could be in part responsible for producing evaporation fluxes with a lower d-excess than might be expected. For example, using values for SMOW ($\delta^{18}\text{O} = 0\text{‰}$, $\delta^2\text{H} = 0\text{‰}$), the water undergoing evaporation has a d-excess of 0‰, but an ocean initial condition of ($\delta^{18}\text{O} = 1\text{‰}$, $\delta^2\text{H} = 1\text{‰}$) has a d-excess of -7‰, which would seem to bring down the d-excess of the evaporative flux by ~7‰ as well.

Reply: Thank you for pointing this out. This was not correctly stated in the manuscript. We changed the text as follows at L. 150:

“We use ECHAM5-wiso ocean surface isotope data (Werner et al. 2011), which is based on an observational dataset for $\delta^{18}\text{O}$ (LeGrande and Schmidt, 2006). The $\delta^2\text{H}$ of sea surface water is assumed to follow the relation of global meteoric waters (Craig and Gordon, 1965) and is thus equal to the $\delta^{18}\text{O}$ multiplied by a factor 8. This setting leads to ocean surface water isotope values in the study region of $\delta^{18}\text{O} \sim -0.2\text{‰}$ and $\delta^2\text{H} \sim -1.6\text{‰}$ and $d \sim 0\text{‰}$.”

We have therefore adjusted the oceanic isotopic composition to -1.6‰ and -0.2‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$, in our air parcel simulations as well. This change in the oceanic composition leads to relatively small changes in the APM simulations. The largest change can be seen in the evolution of d , which shows a smaller decrease with the new ocean composition as expected due to the higher d at the source, but the d decrease is still of the same order of magnitude as before. The figures and text have been updated accordingly.

7. L. 169: there is often a lot of confusion regarding αk , often stemming from whether it is defined based on D_i/D (and hence, $\alpha k < 1$) or D/D_i (hence $\alpha k > 1$) (e.g., Benetti et al., 2014), where D_i is the diffusivity of the isotopologue with a substituted atom (^2H or ^{18}O). Obviously, both can be correct depending on how the equations are cast, but it may be worth specifying

that you are referring to an α_k value based on D_i/D in your work, since the alternative definition is also widely used.

Reply: We added this information to avoid confusion. We now write on lines 199-200:

“ $\alpha_e < 1$ is the equilibrium fractionation factor, $\alpha_k \leq 1$ the non-equilibrium fractionation factor of vapour with respect to liquid. “

8. L. 235: I think the supplemental figures are not numbered in text in the order they appear.

Reply: We adjusted the order of the supplement figures.

9. L. 251-252: I think this sentence could be a bit more clear – clearly rainout could play a role in altering SWIs, but it’s not clear why you might expect to see these at the ocean-water interface if there has been substantial adiabatic lifting (presumably along isentropes, cf. (Bailey et al., 2019)?). Presumably this would be through mixing and/or subsidence, but it’s not made clear here.

Reply: Thank you for pointing out that we can make this point clearer. We don’t expect rainout to occur at the air-sea interface where the measurements took place. But, the isotopic composition of water vapour at the air-sea interface could still be affected by previously occurring cloud processes and downward transport by subsidence or turbulent mixing. For example, free-tropospheric air parcels entrained into the marine boundary layer might show an isotopic signal from cloud-related processes. We adjusted the text on lines 281-285 as follows:

“For air parcels close to the ocean-atmosphere interface, ocean evaporation and dew deposition are expected to be more important for the isotopic composition of water vapour than moist processes related to cloud formation at higher altitudes. Nonetheless, SWIs in near-surface water vapour might carry a signal from up-stream cloud formation, during which a decrease in d_a occurred. This can happen due to near-surface fog formation or due to cloud formation in the boundary layer with subsequent downward transport by subsidence or turbulent mixing.”

10. L. 304 – is THE a misrendered θ_e ? (Also, there appears to be some inconsistency in case: a capital Θ is used in Fig. 5 and L. 340 instead of the lower-case θ used elsewhere)

Reply: Yes, thank you for pointing out this typo, we made the notations consistent throughout the manuscript.

11. L. 437-441 – this is an interesting point! In addition to the mixing process here, I wonder if the more turbulent coupling between the surface and the

near-surface atmosphere could have the effect of altering the ‘effective’ kinetic fractionation factor here as well and alter d independent of mixing, for example by changing the value of the exponent used on the ratio of diffusivities (eq. 5 in (Pfahl & Wernli, 2009), also (e.g., Gat, 1996; Mathieu & Bariac, 1996; Merlivat & Jouzel, 1979; Riley et al., 2002)

Reply: Thank you for highlighting this point. In an earlier publication (Thurnherr et al. 2020), we made use of two continuous measurements of the water vapour isotopic composition at two different heights during the Antarctic Circumnavigation Expedition. The difference between these two measurement time series showed a weak wind dependency that was interpreted as changes in vertical turbulent mixing and different relative importance of sea spray evaporation at the two elevations (see Fig. 10 in Thurnherr et al. 2020).

During the passage of the warm sector from 26 to 28 December 2016, high wind speed, moderate sea spray concentrations and a low wave age was measured near Marion Island. The measured vertical $\delta^{18}\text{O}$ gradient is close to 0‰ over 5.5 m during this period (Fig RC2.1). This could indicate strong vertical mixing close to the air-sea interface with weak influence from sea spray evaporation at both elevations (8 and 13.5 m a.s.l.). Such measurements could also be used to constrain the exponent of the ratio of diffusivities in the non-equilibrium fractionation factor as mentioned in your comment.

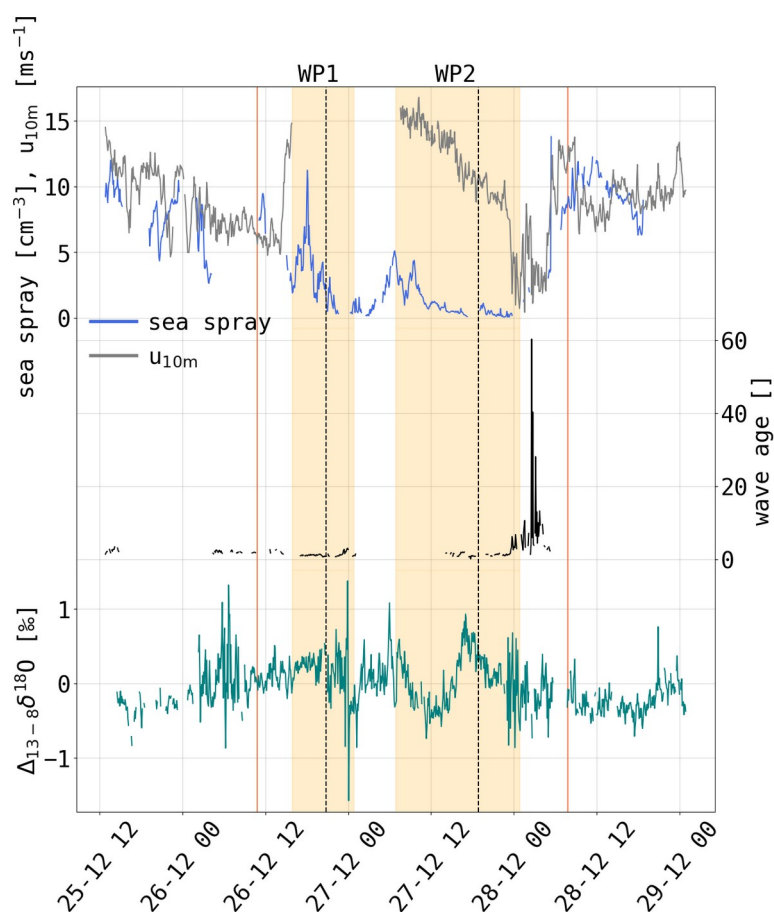


Figure RC2.1: Temporal evolution of measured hourly sea spray concentration (blue line), 10m wind speed (grey line), wave age (black line) and difference in $\delta^{18}\text{O}$ in water vapour between measurements at 8 m and 13.5 m a.s.l. (green line) during ACE from 12 UTC 25 Dec 2016 to 12 UTC 29 Dec 2016. The vertical orange lines denote the beginning and end of the warm temperature advection event. The shaded orange areas correspond to the two periods WP1 and WP2 with low d during supersaturated conditions.

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