# Response to topic editor

We thank the editor for their comments on the revised version of the manuscript. We have addressed all comments below and implemented the changes in a new revised version of the manuscript. The line numbers indicated below correspond to the latest version of the manuscript (revised version after implementation of reviewer's comments). Note that we have also updated the reference to the dataset (now published on PANGAEA).

Black: editor's comment (*italic*: authors response to initial reviewer's comments)

Blue: author's response Green: revised text

#### Reviewer 1:

### You replied to a comment:

> We agree with the reviewer's comment that we used two standards mostly outside of the range of measured isotopic ratios. However, the standard mentioned here by the reviewer (VSAEL) was not yet made available when the calibrations of the instruments were performed in the field. We therefore used the most depleted standard available to us at that time, which was the homemade FP5 standard.

There will be other readers wondering about this. Can you make a note on this in the text with the release date of the VSAEL?

To be exact, the standard VSAEL was existing but not available for calibrations in the field when our instruments were deployed (reserved for specific use in the laboratory). We included a note in the text as follows (l. 163, in bold):

[...] -257.2‰). Note that the very depleted standard VSAEL was not available for calibrations in the field when our instruments were deployed. The calibrations [...]

### You replied to a comment:

> We attribute the different behaviour of the two analysers to the humidity levels. At these low humidities (below 50 ppmv, which is most of the time in March when the two instruments show very different behaviour), the humidity-isotope response calibrations are not constrained for either analyser (lowest calibration point is 50 ppmv, as explained in Sect. 2.2.2). Therefore neither instrument is really reliable at these humidities because the calibration is extrapolated. This is also the reason why we discard this period for the observation-model comparison. However, it seems that this particular Picarro analyser would be best at capturing the atmospheric water vapour isotopic composition at these low humidities, as shown in Figure 6b and c where the diurnal cycle in  $\delta^{18}O$  and  $\delta D$  measured by the Picarro follows the diurnal cycle in the atmospheric humidity (minimum  $\delta^{18}O$  and  $\delta D$  associated with minimum humidity), which is what we expect. In contrast, the AP2E shows an opposite phase between  $\delta^{18}O$  and  $\delta D$  during March. Nevertheless, this does not permit concluding on the ability of the AP2E or Picarro analyser to measure at very low humidity levels, since the data

shown here are only calibrated down to 50 ppmv. Further efforts should be made to better constrain the calibration in order to use the instruments at very low humidities.

A condensed version of this analysis should be added to the text. This could be presented as a qualitative extension of your comparison for when both instruments are outside their calibration range and therefore when quantitative comparison is not possible.

We added a condensed version of this analysis to the manuscript (after 1. 486, in bold below):

[...] and make available in public access only this part of the dataset in Landais et al. (2024b) for future work.

After mid-February, it seems that this particular Picarro analyser best captures the atmospheric water vapour isotopic composition at these low humidities. As shown in Figure 6b and c, the diurnal cycle in  $\delta^{18}O$  and  $\delta D$  measured by the Picarro follows the diurnal cycle in the atmospheric humidity (minimum  $\delta^{18}O$  and  $\delta D$  associated with minimum humidity), which is what we expect. In contrast, the AP2E analyser shows an opposite phase between the humidity and the  $\delta$ -values. Nevertheless, this does not permit concluding on the ability of the AP2E or Picarro analyser to measure at very low humidity levels, since the data shown here are only calibrated down to 50 ppmv (Sect. 2.2.2). Further efforts should be made to better constrain the calibration in order to use the instruments at very low humidities.

#### Reviewer 2:

### Comment 9, you replied:

> Yes, this is a correct observation. We modified the text to make our point clearer as follows (l. 30–36, in bold):

In polar ice cores,  $\delta^{18}O$  and  $\delta D$  have traditionally been interpreted as a temperature proxy based on empirical relationships between the mean annual temperature and the isotopic composition of snow samples (e.g. Johnsen et al., 1992; Jouzel et al., 2007; Lorius et al., 1979). Alongside, d-excess has been interpreted as a proxy for climatic conditions at the evaporative source region (e.g. Landais et al., 2021; Stenni et al., 2010; Uemura et al., 2008; Vimeux et al., 1999). However, an increasing number of studies have shown that the isotopic composition ( $\delta^{18}O$ ,  $\delta D$ , and d-excess) of the snow surface and deeper layers in the snowpack is affected by post-depositional processes at the ice sheet surface (e.g. Casado et al., 2018, 2021; Ollivier et al., 2025; Steen-Larsen et al., 2014; Town et al., 2024; Zuhr et al., 2023).

I agree with the reviewer that it is not clear why there is opposition between the two parts of your statement (marked by "however"). If the relation between isotopic composition measured in ice cores and temperature was derived empirically, then it already includes the postdepositional processes and there is no reason to present the postdepositional processes as contradicting established proxies. If, on the contrary, the studies you mention highlight shortcomings in established relationships stemming from postdepositional processes (dating uncertainty, removal or migration of peaks in isotopic profiles...), then please be more specific about what they are. It is a good opportunity to introduce how

your high-quality surface measurements are necessary to better understand the link between atmospheric state and ice core records.

We agree with both the reviewer and the editor that the opposition term "however" is misleading here. We have replaced it by the term "In the last decade" (1. 33-35, in bold below):

[...] evaporative source region (e.g. Landais et al., 2021; Stenni et al., 2010; Uemura et al., 2008; Vimeux et al., 1999). In the last decade, an increasing number of studies have shown that the isotopic composition ( $\delta^{18}$ O,  $\delta$ D, and d-excess) [...]

The two following sentences then emphasize on the importance of measurements of the atmospheric water vapor isotopic composition.

# Comment 10, you replied:

> The method used in Leroy-Dos Santos to estimate the uncertainty is different from the method we used in our manuscript, so it is a bit delicate to compare directly. Nevertheless, they estimate the uncertainty on  $\delta^{18}O$  to be approximately 2.5% when the humidity is maximal (between 400 and 600 ppmv, their Figure 7) and close to 4.5% when the humidity is minimal (around 200 ppmv, their Figure 7). In our study, we find the uncertainty on the  $\delta^{18}O$  measured by the Picarro to be between 0.3% at 1000 ppmv (approximate maximum value during the studied time period) and 1.5% at 200 ppmv. Both values were calculated with Equation 4 and the values of  $\sigma(1)$ + in Table 4.

Has this been added to the main text?

We added this information to the text (1. 398, in bold below):

[...] both analysers presented along the data in the following section. For comparison, the uncertainty on  $\delta^{18}O$  estimated by Leroy-Dos Santos et al. (2021) is approximately 2.5‰ when the humidity is maximal (between 400 and 600 ppmv, their Fig. 7) and close to 4.5‰ when the humidity is minimal (around 200 ppmv, their Fig. 7). Although our estimation method is different, we find here the uncertainty on the  $\delta^{18}O$  measured by the Picarro to be between 0.3‰ at 1000 ppmv (approximate maximum value during the studied time period) and 1.5‰ at 200 ppmv. Both values were calculated with Equation 4 and the values of  $\sigma_{i,drift}$  in Table 4.

### Comment 16. Websites' URL:

Footnotes should be avoided, please make it a reference to a webpage: <a href="https://www.earth-system-science-data.net/submission.html#references">https://www.earth-system-science-data.net/submission.html#references</a>

We modified the text to the following (1.91-100, in bold below):

A Picarro L2130-i analyser (Picarro Inc., CRDS measurement technique, Picarro analyser hereinafter; **Picarro, 2025**) [...] In parallel to the Picarro analyser, a prototype (non commercially available) of a

AP2E ProCeas analyser (AP2E Inc., OF-CEAS measurement technique, AP2E analyser hereinafter; **AP2E**, **2025**) [...]

And added the references to the reference list as follows:

Picarro:

https://www.picarro.com/environmental/products/l2130i\_isotope\_and\_gas\_concentration\_analyzer, last access: 19 September 2025

AP2E: https://www.ap2e.com/en/our-gas-analyzers/proceas/, last access: 19 September 2025

# Comment 21, you replied:

> We conducted 9 individual calibrations, each associated with a single humidity level (the humidity does not vary within each calibration). Each calibration lasts about two hours, and we average the last 10 minutes to get each data point. This way, we minimize the memory effect by ensuring that potential residual water from previous calibrations has been evacuated from the system and that the humidity level has reached a stable state. In addition, compared to measurement uncertainty, the memory effect is negligible at 200 ppmv. Nevertheless, memory effect is the reason why we do not go below 50 ppmv for the calibration steps, as the residual water is not negligible. In Figure 3, the calibration humidities are different for both instruments because we show the raw humidity. As explained in our answer to comment n°19 above, we do not calibrate the isotopes with the calibrated humidity but with the measured humidity, to prevent incorporating an additional error. Therefore both instruments, although the target calibration humidity is the same, will not measure the same humidity and not the precise target humidity (that is why it also appears as random values).

We have added the information about the number of calibrations in the text as follows (l. 135): [...] performing one series of nine calibrations in January 2024.

Please add information about the calibration duration and the assumption that memory effect is negligible at 200 ppmv to the text.

## We added this information to the text (l. 146, in bold below):

[...] The calibration steps were performed from high to low humidity (humidities ranging from 1100 to 50 ppmv). Each calibration lasts approximately two hours, and the data point correspond to the average of the last 10 minutes, in order to minimize the memory effect. We assume that at 200 ppmv, the memory effect is negligible compared to the measurement uncertainty. The humidity levels [...]

#### Comments 31 & 32:

Is there a clear statement somewhere in the text saying that the humidity-isotope response is

known/expected to be instrument-dependent?

## Yes, this statement is made 1. 134-135:

"This humidity-isotope response is instrument-specific (e.g. Steen-Larsen et al., 2013) and is dependent on the isotopic composition of the laboratory standard used to perform the calibrations (e.g. Lauwers et al., 2025; Weng et al., 2020)."

#### And 1. 282-284:

"The difference in humidity-isotope response of the two Picarro analysers (HIDS2319 and HIDS2308) is not surprising since different spectrometers will have a different humidity-isotope response (e.g. Steen-Larsen et al., 2013)."

## Comment 34:

I agree that the  $2\sigma$  ranges are hard to read. Please replace them with vertical whiskers on the right-hand side of each panel. Please add a red marker for outliers in the legend. The legend of the three panels could be merged and placed at the top of the figure.

We have modified Figure 4 and its caption to include the editor's comment:

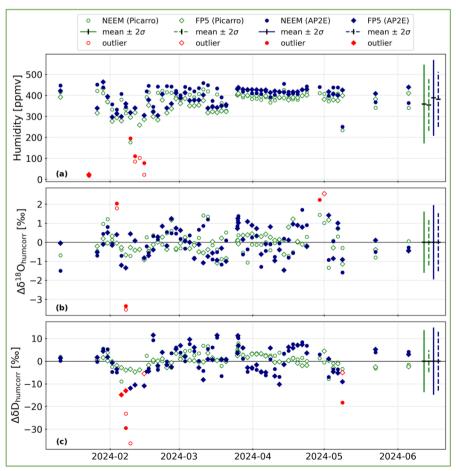


Figure 4: Results of the regular calibrations performed with two laboratory standards (FP5 and NEEM) between

January 11th and June 6th with the new version of the LHLG (description in Sect. 2.2.2 and 2.2.3). Panel (a) shows the humidity measured by both analysers during each calibration. The red markers show the calibrations that were discarded (outside of two standards deviations around the mean humidity, **indicated by the vertical bars on the right-hand side**). Panels (b) and (c) show the measured isotopic ratios, corrected for the humidity-isotope response (Sect. 2.2.2 and 3.1.2), by both analysers during each calibration as a deviation of the mean over the whole period ( $\Delta \delta^* = \delta_{i,humcorr} - \overline{\delta_{i,humcorr}}$ , subscript  $_i$  is for each isotope species). The isotopic ratios of each calibration are corrected for the isotope-humidity response of each analyser. In panels (b) and (c), only the accepted calibration from panel (a) are shown. The red markers show the calibrations that are discarded in a second step (outside of two standard deviations around the mean isotopic ratio, **indicated by vertical bars on the right-hand side**).

## Comment 37:

The RMSE annotations seem quite out of place. Either mention them in the text only or alternatively: - move the RMSE to the legend where instrument name, linear equation, and RMSE are each on a new line

- potentially move the legend outside (e.g. on top of) the plotting area and reduce the size of the panel Please add panel labels.

We have modified Figure 5 and its caption to include the editor's comment:

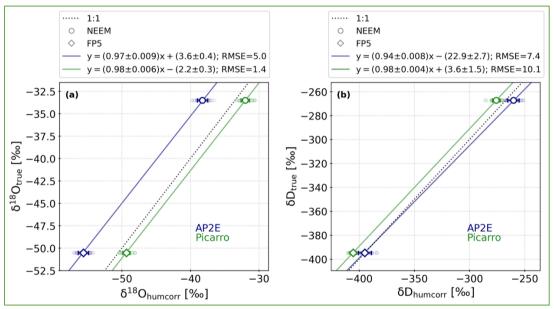


Figure 5: Humidity-isotope corrected ratios vs true isotopic ratios ( $\delta^{18}$ O in panel (a) and  $\delta$ D in panel (b)) of two laboratory standards (FP5 and NEEM) for both Picarro and AP2E analysers. In both panels, the smaller coloured markers represent all selected calibrations and the larger coloured markers the average isotopic ratio of all selected calibrations (whiskers represent one standard deviation). The coloured lines show the linear regressions between the true and humidity-corrected isotopic ratios using the two laboratory standards.

#### Comment 40:

I believe there is now too much information in Figure 6 and statistics look like small tables inserted in a plot. Please make a clearer distinction between quantifying the impact of calibration (which should be done before section 3.2) and presenting your final calibrated values with their derived uncertainties

(which is section 3.2 and Figure 6). Prior to section 3.2, you should present the raw vs calibrated statistics either in a table or in scatter plots (e.g. additional panels in Figure 5) and discuss them there. When coming to section 3.2 and Figure 6, the focus should be on the temporal evolution of the calibrated values, their uncertainties, and how they differ for the two instruments. Again, the grey statistics in Figure 6 should either be in a table or shown on a scatter plot (potentially as additional, squared panels displayed on the right-hand side of each time series plot in Figure 6), so there is no doubt about which series are being compared.

We argue that the presentation and comparison of the raw and calibrated data should still be included in Section 3.2, since Section 3.1 is presenting the results of the calibration steps themselves. However, we do agree that is should be clearer when we discuss the effect of the calibration on the data and the instrument inter-comparison. In addition, we agree that the statistics inserted in Figure 6 makes the figure hard to read. To accommodate for the different issues, we modified the manuscript by:

- Adding two sub-sections in Section 3.2:
  - o 3.2.1 Calibration effect on measured time series includes text from 1. 438 to 463
  - o 3.2.2 Instrument inter-comparison includes text from 1. 465 to 495
- Removing the statistics inserted in Figure 6 and adding two tables to the text:
  - Table 5 in new Section 3.2.1 with statistics for the comparison raw calibrated time series
  - Table 6 in new Section 3.2.2 with statistics for the instrumental inter-comparison of the two calibrated time series

# The Section 3.2 is now the following (excluding Figures 6 and 7, bold indicates new/modified text):

## 3.2 Time series of the water vapor isotopic composition

Figure 6 shows the evolution of the atmospheric humidity,  $\delta^{18}$ O,  $\delta$ D and d-excess measured by both laser spectrometers between December 2023 and March 15th 2024. Figure 7 shows a focus on a four-day period in January 2024 (corresponding to the grey hatched area in Fig. 6). Note that the time series are not continuous, with interruptions due to calibration periods, maintenance work on the instruments or electrical shutdowns. Missing data represents 21% of the overall dataset (December 6th 2023 to March 15th 2024). The air temperature shown in Fig. 7 is measured at 1.5 m above the surface by an Automatic Weather Station (AWS) installed in the vicinity of Concordia station (Grigioni et al., 2022). The comparison of the raw and calibrated time series from the Picarro and AP2E analysers is described in Sect. 3.2.1 and statistics over the whole period are summarized in Table 5. The instrument inter-comparison of the calibrated time series from the two analysers is described in Sect. 3.2.2 and statistics over the whole period are summarized in Table 6.

### 3.2.1 Calibration effect on measured time series

The raw humidity measured by both analysers show the same variations over the whole period (Fig. 6a and 7a), except for a bias already identified in Sect. 3.1.1. After the calibration against the independent humidity sensor, the humidities are in excellent agreement over the whole period (**Table 5**). The calibrated humidities are showing the same diurnal variations for both analysers, synchronous

with the temperature diurnal cycle on site (Fig. 7a). In addition, both instruments record the decrease of the humidity from the beginning of February, coinciding with the onset of the winter at Dome C (Fig. 6a).

Contrary to the humidity, the calibration of the raw data has a significant effect on the  $\delta^{18}$ O time series of both analysers. For the AP2E analyser, the calibration of the raw  $\delta^{18}$ O time series shifts it towards higher values (Fig. 6b and 7b), with a mean difference of 9.2% over the whole period between the raw and calibrated time series (Table 5). This shift is expected from the absolute calibration curve (Sect. 3.1.3). The amplitude of the diurnal cycle is also slightly reduced after applying the calibration (Fig. 7b), due to the humidity- $\delta^{18}$ O response of the analyser (i.e. positive correction for low humidities and negative correction for high humidities, Sect. 3.1.2). For the Picarro analyser, the raw and calibrated  $\delta^{18}$ O time series show a mean difference of -9.3% (**Table 5**), which is mostly due to the part of the time series from beginning of February onwards. The amplitude of the diurnal cycle is larger after calibration, as expected from the humidity- $\delta^{18}$ O response of the Picarro which shows negative correction for lower humidities (Fig. 3a, Sect. 3.1.2). This is further visible on the period from the end of January onwards, where the diurnal cycles show an opposite behaviour between the raw and calibrated data: the raw data is in opposite phase to the humidity (minimum  $\delta^{18}$ O associated with maximum humidity) and the calibrated data is in phase with the humidity (minimum  $\delta^{18}$ O associated with minimum humidity). This is an effect of the large humidity- $\delta^{18}$ O response of the Picarro at low humidities (Fig. 3a, Sect. 3.1.2).

Compared to  $\delta^{18}$ O, the raw and calibrated  $\delta D$  time series from both instruments are rather similar, at least during the period where the humidity is above 200 ppmv (mid-December to end of January, Fig. 6c). The calibration of both analysers modifies the average  $\delta D$  values (mean difference of 7.4% for the Picarro and 19.1% for the AP2E analyser over the whole period, **Table 5**). The calibration of the  $\delta D$  time series does not affect the amplitude of the diurnal cycle for neither analyser (Fig. 7c). Both raw  $\delta D$  time series compare relatively well from mid-December to the end of January (dashed lines in Fig. 6c), with the same in-phase relationship between  $\delta D$  and the mixing ratio as for the calibrated  $\delta^{18}O$  time series. This in-phase relationship between  $\delta D$  and the humidity is preserved after calibration (plain lines in Fig. 6c and 7c).

Table 5. Root mean square difference (RMSD), mean difference (MD), mean absolute difference (MAD) and squared Pearson correlation coefficients (R<sup>2</sup>) between the raw and calibrated time series of the Picarro and AP2E analysers. MD is calculated as calibrated – raw. All statistics are calculated using the data between December 6th 2023 and March 15th 2024.

|                              | parameter               | RMSD      | MD        | MAD             | $\mathbb{R}^2$ |
|------------------------------|-------------------------|-----------|-----------|-----------------|----------------|
| Picarro raw vs calibrated    | humidity                | 26.8 ppmv | 23.6 ppmv | 23.6 ppmv       | 1.0            |
|                              | $\delta^{18}O$          | 17.8‰     | -9.3‰     | 9.3‰            | 0.49           |
|                              | δD                      | 13.2%     | 7.4%      | 11.8‰           | 0.98           |
|                              | d-excess                | 137.2%    | 81.9‰     | 81.9‰           | 0.53           |
| AP2E<br>raw vs<br>calibrated | humidity                | 2.6 ppmv  | 1.5 ppmv  | <b>2.3 ppmv</b> | 1.0            |
|                              | $\delta^{18}\mathrm{O}$ | 10.5‰     | 9.2%      | 9.2‰            | 0.84           |
|                              | δD                      | 28.6‰     | 19.1‰     | 19.1‰           | 0.97           |
|                              | d-excess                | 58.2%     | -54.4‰    | 54.4%           | 0.77           |

# 3.2.2 Instrument inter-comparison

There is a good agreement between the  $\delta^{18}$ O calibrated time series from the AP2E and Picarro analysers over the period, until they start to diverge mid-February (Fig. 6b). Considering the entire period, the two  $\delta^{18}$ O calibrated time series show a mean absolute difference of 3.6% (**Table 6**), which is within the range of uncertainties of the calibrated time series (shaded areas in Fig. 6b), and a squared Pearson correlation coefficient R<sup>2</sup> of 0.58 (**Table 6**). When considering only the period before mid-February, the mean absolute difference is reduced to 1.8% and R<sup>2</sup> is improved to 0.8 (not shown). The good agreement between the two analysers confirms that the calibration is valid for the range of humidities encountered over this period.

As for  $\delta^{18}$ O, we observe that the calibrated  $\delta$ D time series from both instruments agree well between mid-December to mid-February, when similarly to  $\delta^{18}$ O they start to diverge (Fig. 6c). Over the entire period, the mean absolute difference between the two calibrated  $\delta$ D time series is 22.1% (**Table 6**), which is also within the uncertainty of both calibrated time series (shaded areas in Fig. 6c), and R<sup>2</sup> is 0.59 (Fig. 6c). When considering only the period before mid-February, the mean absolute difference is reduced to 10.7% and R<sup>2</sup> is improved to 0.85 (not shown).

Finally, the raw time series of d-excess are very different between the two analysers (Fig. 6d and 7d). However, after the calibration of both analysers, the two d-excess time series are comparable within their uncertainty range (Fig. 6d and 7d), with a mean absolute difference of 27.7‰ (Table 6). As for  $\delta^{18}$ O and  $\delta$ D, the calibrated d-excess time series of the two analysers diverge from mid-February onwards (Fig. 6d).

[...]

Table 6. Root mean square difference (RMSD), mean difference (MD), mean absolute difference (MAD) and squared Pearson correlation coefficients (R<sup>2</sup>) between the two calibrated time series of the Picarro and AP2E analysers. MD is calculated as Picarro – AP2E. All statistics are calculated using the data between December 6th 2023 and March 15th 2024.

| parameter               | RMSD     | MD        | MAD             | $\mathbb{R}^2$ |
|-------------------------|----------|-----------|-----------------|----------------|
| humidity                | 4.5 ppmv | -1.0 ppmv | <b>2.7 ppmv</b> | 1.0            |
| $\delta^{18}\mathrm{O}$ | 6.7‰     | -3.5‰     | 3.6‰            | 0.58           |
| δD                      | 39.6‰    | -9.8‰     | 22.1‰           | 0.59           |
| d-excess                | 54.4%    | 18.6‰     | 27.7‰           | 0.02           |

Is it because of different temporal span or because of calibration that the statistics in grey in the first panel do not match with the statistics from Figure 2c?

It is both due to a different temporal span and the comparison between different datasets. The statistics in Figure 2c correspond to the comparison between the raw humidity time series measured by the Picarro and the AP2E analysers over the period January 1st to March 15th 2024. In Figure 6a, the statisctics correspond to the comparison between the calibrated humidity time series measured by the

Picarro and AP2E analysers over the period December 6th 2023 to March 15th 2024.

Figure 8: Same issue. Either make the statistics a separate table or show them with a scatter plot (potentially as additional panels on the right-hand side of the time series plots in Figure 8).

We removed the statistics from Figure 8 and included a new table in Section 3.3 (l. 503-530, bold indicates new/modified text):

[...]. Table 7 summarizes the statistics of the comparison between the modelled and calibrated time series from the Picarro and AP2E analysers.

The comparison of the humidity modelled by LMDZ6-iso and measured by both analysers shows an overall good agreement albeit a positive bias in the model (**Fig. 8a and Table 7**), including in terms of the amplitude of the observed diurnal cycle (Fig. 8a and 9a). However, during some specific periods, the model shows higher humidity levels than what is observed, especially during the nighttime (e.g. December 16th to 20th, light brown area in Fig. 8a). Contrary to the humidity, the air temperature modelled by LMDZ does not exhibit any mean bias compared to the air temperature measured by the local AWS (MD = -0.6°C and MAD = 2.8°C, not shown).

Although the model reproduces the observed in-phase relationship between  $\delta^{18}$ O and the humidity, the comparison between the modelled and observed  $\delta 18$ O shows a poorer agreement than for humidity. Firstly, the modelled  $\delta^{18}$ O shows an overall positive bias over the entire period compared to the observations, with a mean difference of 4.9% compared to the Picarro analyser and 3.0% compared to the AP2E analyser (**Table 7**). Secondly, the amplitude of the diurnal cycle modelled by LMDZ6-iso is overall larger than in the observations (Fig. 8b). Over the period January 11th to January 15th 2024 (Fig. 9b), the amplitude of the mean diurnal cycle in  $\delta^{18}$ O modelled by LMDZ6-iso is 10.9% (from -70.9 to -60.0%, not shown), higher than the one from both the Picarro analyser (5.7%, Sect. 3.2) and the AP2E analyser (4.7%, Sect. 3.2).

The same patterns are observed for  $\delta D$ . The modelled  $\delta D$  also shows an overall mean positive bias compared to the observations, with a mean difference of 27.3% compared to the Picarro analyser and 19.4% compared to the AP2E analyser (**Table 7**). The amplitude of the diurnal cycle is also larger in LMDZ6-iso than in the observations (Fig. 8c). Between January 11th and January 15th 2024 (Fig. 9c), the mean diurnal amplitude modelled by LMDZ6-iso is 69.0% (from -515.8 to -446.8%, not shown), which is higher than the observed one (34.9% for Picarro analyser, 29.5% for AP2E analyser, Sect. 3.2).

Lastly, due to the biases identified for  $\delta^{18}O$  and  $\delta D$ , the d-excess modelled by LMDZ6-iso also shows some discrepancies with the observations. The model shows an overall negative bias compared to the observations, with a mean difference over the whole period of 12.1% compared to the Picarro analyser and of 4.6% compared to the AP2E analyser (**Table 7**). The comparison of the amplitudes of the diurnal cycle is less conclusive than for  $\delta^{18}O$  and  $\delta D$ , due to the large uncertainties associated with the observations (Fig. 9d). However, we observe that the model still correctly captures the observed antiphase relationship between d-excess and  $\delta^{18}O$  (or  $\delta D$ ), with a maximum d-excess when  $\delta^{18}O$  is minimal, i.e. during the night, and a minimum d-excess when  $\delta^{18}O$  is maximal, i.e. during the day (Fig.

Table 7. Root mean square difference (RMSD), mean difference (MD), mean absolute difference (MAD) and squared Pearson correlation coefficients ( $R^2$ ) between the calibrated time series of the Picarro and AP2E analysers and the modelled time series by LMDZ6-iso. MD is calculated as model – observations. All statistics are calculated using the data between December 6th 2023 and February 14th 2024.

|                         | parameter           | RMSD      | MD        | MAD       | $\mathbb{R}^2$ |
|-------------------------|---------------------|-----------|-----------|-----------|----------------|
| LMDZ6-iso vs<br>Picarro | humidity            | 94.9 ppmv | 36.0 ppmv | 69.9 ppmv | 0.82           |
|                         | $\delta^{18}$ O     | 6.8‰      | 4.9‰      | 6.0%      | 0.45           |
|                         | $\delta { m D}$     | 40.1‰     | 27.3‰     | 35.0‰     | 0.49           |
|                         | d-excess            | 15.8‰     | -12.1‰    | 13.7‰     | 0.25           |
|                         | humidity            | 90.2 ppmv | 29.0 ppmv | 66.5 ppmv | 0.83           |
| LMDZ6-iso vs            | $\delta^{18}{ m O}$ | 6.4‰      | 3.0%      | 5.5‰      | 0.23           |
| AP2E                    | $\delta { m D}$     | 37.9‰     | 19.4‰     | 32.3‰     | 0.35           |
|                         | d-excess            | 21.0%     | -4.6%     | 17.0%     | 0.0            |