Measurements of isotopic composition of vapour on the Antarctic Plateau – Supplementary materials

1. Calibration device

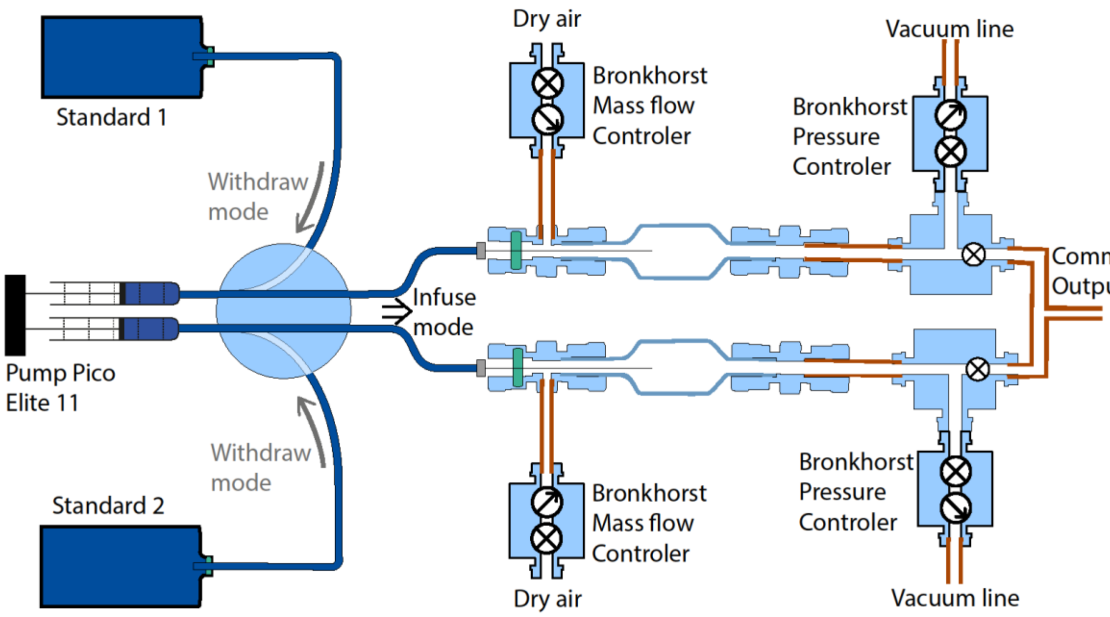

Figure S1: Schematic of the humidity generator used as a calibration device. A pump Pico Elite 11 pushes water through a double 6 ways valve into a needle in an evaporation chamber where a dry air flow is created. This enables controling the humidity of the moist air formed by mixing the water and the dry air directly.

Standard calibration devices cannot be used to produce humidity levels as low as the one encountered on the Antarctic Plateau (under 1000 ppmv). We therefore built our own calibration device in order to produce vapour with known isotopic composition at low concentration. This home-made calibration device consists of an infuse/withdraw pump 11 elite from Harvard Apparatus, which can produce a water flow as low as 3.66pl/min with an accuracy is of the order of 0.5%. This pump pushes water through a needle toward an evaporation chamber with a controlled dry air laminar flow. The airflow can be controlled between 0 and 500 standard cubic centimetre per minute (sccm) with a precision of 4 sccm over a pressure range from 100 to 1000 hPa by Bronkhorst devices. The main improvement for this version of the calibration device is the integration of a 3 ways liquid valve which enables one to switch between a withdraw and an infuse mode to either pump water from a reservoir or push it toward the needle. Apart from the obvious convenience brought by this addition, the valve is connecting the syringe, the water reservoir and the needle with air tight connexions increasing the robustness and successfully eliminating the presence of air bubbles in the water sampled by the syringe.

When a water drop forms at the tip of the needle, the diameter of the drop is transiently adjusted up to the point when the inflow of liquid water in the needle is compensated by evaporation: at this stage, the drop remains at the tip of the needle and a constant flow of vapour is produced. When the permanent regime is reached (within a few minutes), the isotopic composition of the evaporated vapour is exactly the isotopic composition of the water injected, and the humidity level is completely controlled by the inflows of liquid water and air, therefore independent of local thermodynamic properties such as temperature or pressure. By propagating the uncertainty for the air fluxes (1%) and water flux (0.5%) to the conversion formula to calculate the humidity, we estimate the uncertainty associated with this humidity production of the order of 2%. Experimentally, standard deviation on the specific humidity measured during the different sets of calibration is usually between 1 and 5 ppmv. This leads to an uncertainty of 1 to 2% of the specific humidity. The production of humidity by the calibration device is therefore more precise than the measurements of the Picarro and HIFI.

2. Humidity calibration

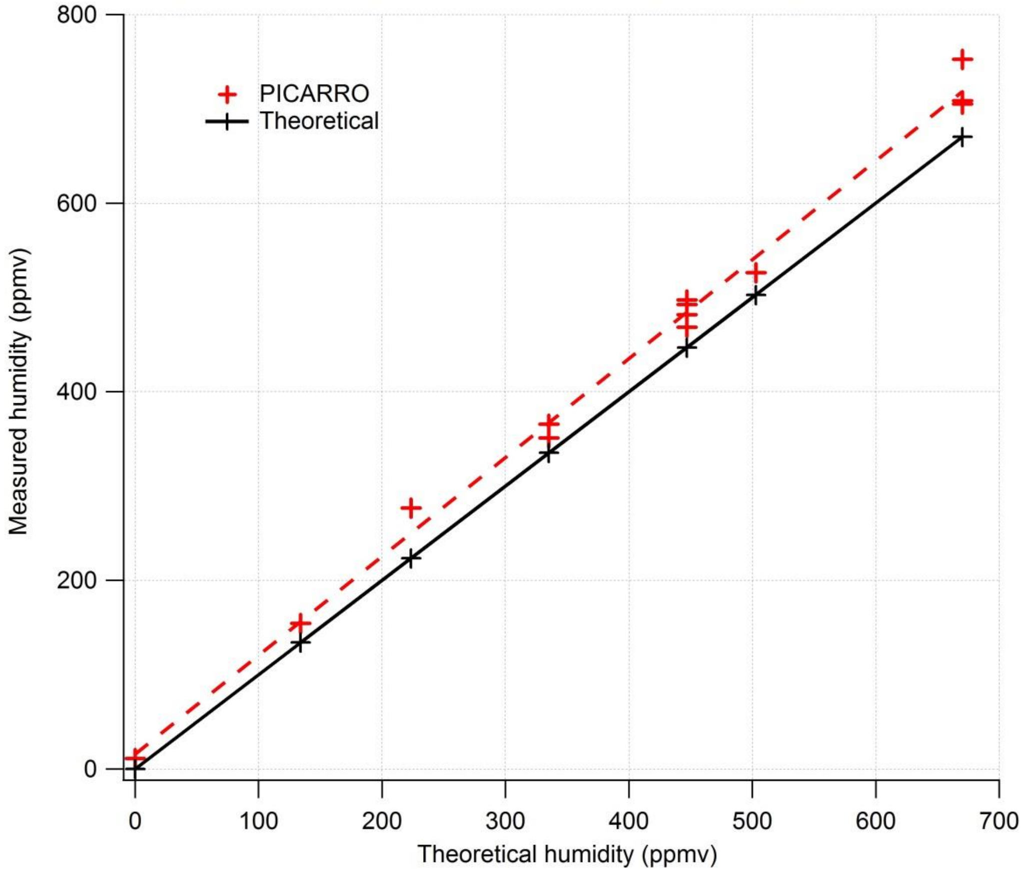

Figure S2: Measured humidity by the Picarro (red crosses, data and dashed lined, fit) on the field compared to the theoretical produced humidity by the calibration device (black line).

Infrared spectrometers humidity measurements are not absolute and also have to be calibrated against trustworthy humidity etalon. Usually, dew points generators provide the best performances to create known stable humidity but they cannot be used for humidity levels corresponding to saturated vapour pressure under 0°C. Here, we used the calibration device which is physically dominated by the fluxes of liquid water and air sent to the instrument to produce known stable humidity.

There is a linear bias between the humidity measurement and the produced theoretical humidity which stands around 7% of the total value. This linear bias has been taken into account and the humidity measurements presented in the main manuscript have a typical uncertainty of 2%.

3. Richardson number

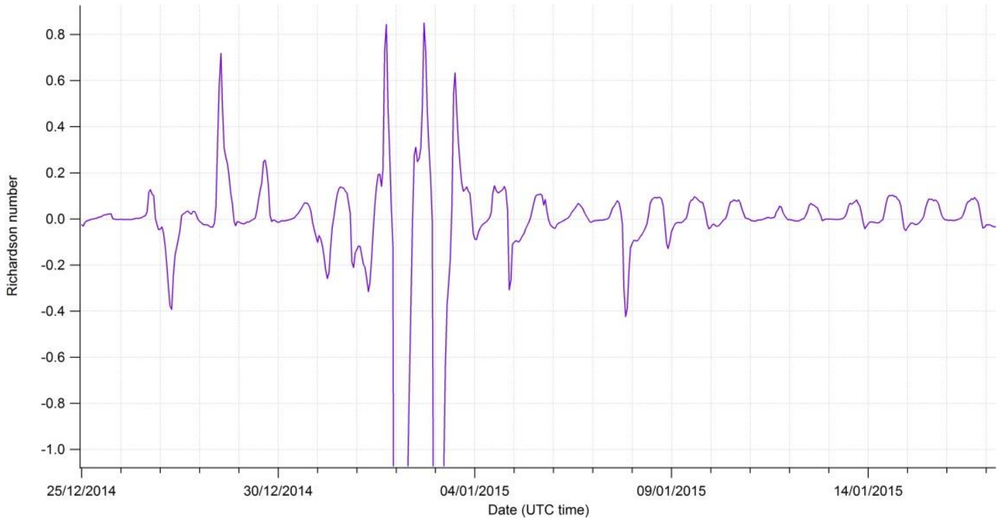

Figure S3: Richardson number at the ground level during the campaign

Erratic behaviour of the Richardson number during regime 1 (from December the 25^{th} to January the 4^{th}) indicates a weakened turbulent mixing of the first meters of the atmosphere compared to regime 2 (after January the 4^{th}).