Abrupt excursion in water vapor isotopic variability during cold fronts at the Pointe Benedicte observatory in Amsterdam Island

Amaëlle Landais¹*, Cécile Agosta¹*, Françoise Vimeux¹², Olivier Magand³, Cyrielle Solis¹, Alexandre Cauquoin⁴, Niels Dutrievoz⁴, Camille Risi⁵, Christophe Leroy-Dos Santos¹, Elise Fourré¹, Olivier Cattani¹, Olivier Jossoud¹, Bénédicte Minster¹, Frédéric Prié¹, Mathieu Casado¹, Aurélien Dommergue⁶, Yann Bertrand⁶, Martin Werner⁷

¹ Laboratoire des Sciences du Climat et de l’Environnement, LSCE/IPSL, CEA-CNRS-UVSQ, Université Paris-Saclay, 91191 Gif-sur-Yvette, France
² HydroSciences Montpellier (HSM), UMR 5569 (UM, CNRS, IRD), 34095 Montpellier, France
³ Observatoire des Sciences de l’Univers à La Réunion (OSU-R), UAR 3365, CNRS, Université de La Réunion, Météo France, 97744 Saint-Denis, La Réunion, France
⁴ Institute of Industrial Science (IIS), The University of Tokyo, Kashiwa, Japan.
⁵ Laboratoire de Météorologie Dynamique, Institut Pierre - Simon Laplace, Sorbonne Université / CNRS / École Polytechnique – IPP, Paris, France
⁶ Univ. Grenoble Alpes, CNRS, INRAE, IRD, Grenoble INP*, IGE, 38000 Grenoble, France
⁷ Alfred Wegener Institute, Helmholtz Centre for Marine and Polar Research, D-27570 Bremerhaven, Germany

* corresponding authors who contributed equally to the study: amaelle.landais@lsce.ipsl.fr and cecile.agosta@lsce.ipsl.fr
Abstract

In order to complement the picture of the atmospheric water cycle in the Southern Ocean, we have continuously monitored water vapor isotopes since January 2020 in Amsterdam Island (37.7983 °S, 77.5378 °E) in the Indian Ocean. We present here the first 2-year-long water vapor isotopic record monitored on this site. We show that the vapor isotopic composition largely follows the vapor mixing ratio, as expected in marine boundary layers. However, we evidence 11 cold front periods of a few days where there is a strong loss of correlation between water vapor δ18O and mixing ratio. These periods are associated with abrupt negative excursions of water vapor δ18O, often occurring toward the end of precipitation events. Six of these events show a decrease in gaseous elemental mercury suggesting subsidence of air from higher altitude.

Accurately representing the water isotopic signal during these cold fronts is a real challenge for the atmospheric components of Earth System models equipped with water isotopes. While the ECHAM6-wiso model was able to reproduce most of the sharp negative water vapor δ18O excursions, the LMDZ-iso model at 2° (3°) resolution was only able to reproduce 7 (1) of the negative excursions. Based on a detail model-data comparison, we conclude that the most plausible explanations for such isotopic excursions are rain-vapor interactions associated with subsidence at the rear of a precipitation event.
1. Introduction

The main sources of uncertainty in the atmospheric components of Earth System Models for future climate projections are associated with complex atmospheric processes, particularly those related to water vapor and clouds (Sherwood et al., 2014; Arias et al., 2021). Decreasing these uncertainties is of vital interest as the hydrological cycle is a fundamental element of the climate system because it allows, via the transport of water vapor, to ensure the Earth’s thermal balance.

Stable water isotopes are a useful tool to study the influence of dynamical processes on the water budget at various spatial and temporal scales. They provide a framework for analyzing moist processes over a range of time scales from large-scale moisture transport to cloud formation, precipitation, and small-scale turbulent mixing (Galewsky et al., 2016; Thurnherr et al., 2020; Bailey et al., 2023; Dahinden et al., 2021).

The relative abundance of heavy and light isotopes in different water reservoirs is altered during phase change processes due to isotopic fractionation (caused by a difference in saturation vapor pressure and molecular diffusivity in the air and the ice). Each time a phase change occurs, the relative abundance of water vapor isotopes is altered. We express the abundance of the heavy isotopes D and $^{18}$O with respect to the amount of light isotopes $^{16}$O and H in the water molecules through the notation $\delta$:

$$\delta^{18}O = \left( \frac{^{18}O/^{16}O}_{\text{Sample}} / \frac{^{18}O/^{16}O}_{\text{VSMOW}} \right) - 1 \times 1000 \quad \text{(Eq. 1)}$$

$$\delta D = \left( \frac{D/H}_{\text{Sample}} / \frac{D/H}_{\text{VSMOW}} \right) - 1 \times 1000 \quad \text{(Eq. 2)}$$

where VSMOW (Vienna Standard Mean Ocean Water) is an international reference standard for water isotopes.

There are two types of isotopic fractionation: equilibrium fractionation, which is caused by the difference in saturation vapor pressure of different isotopes, and non-equilibrium fractionation, which occurs due to molecular diffusion (e.g. during ocean evaporation in undersaturated atmosphere or snowflakes condensation in oversaturated atmosphere). In the water vapor above the ocean, the proportion of non-equilibrium fractionation, and hence diffusive processes can
be estimated by the deuterium excess, a second order isotopic variable denoted d-excess, defined as (Dansgaard, 1964):

\[ \text{d-excess} = \delta D - 8 \times \delta^{18}O \]  
(Eq. 3)

Over the recent years and thanks to the development of optical spectroscopy enabling continuous measurements of water isotopes ratios in water vapor, an increasing number of studies have focused on the use of stable isotopes in water vapor to document the dynamic of the water cycle over synoptic weather events, such as cyclones, cold fronts, atmospheric rivers (Tremoy et al., 2014; Aemisegger et al., 2015; Munksgaard et al., 2015; Dütsch et al., 2016; Graf et al., 2019; Lee et al., 2019; Ansari et al., 2020; Bhattacharya et al., 2022) or water cycle processes such as water cycle processes such as evaporation over the ocean or deep convection (Bonne et al., 2019; Benetti et al., 2015). For this objective, several instruments have been installed either in observatory stations (e.g. Tremoy et al., 2012; Guilpart et al., 2017; Steen-Larsen et al., 2013; Leroy-Dos Santos et al., 2020; Aemisegger et al., 2012) or on boat (e.g. Thurnherr et al., 2019; Benetti et al., 2014). In the aforementioned studies, the interpretation of the isotopic records is often performed using a hierarchy of isotopic models, from conceptual models (Rayleigh type) to general circulation models or regional weather prediction models equipped with water isotopes (Risi et al., 2010; Werner et al., 2011; Ciais and Jouzel, 1994; Markle and Steig, 2022). Such data comparison enables one to test the performances of the models either in the simulation of the dynamic of the atmospheric water cycle or in the implementation of the water isotopes.

Our study is part of these dynamics analyses and aims at improving the documentation of climate and water cycle in the Southern Indian Ocean. This region is poorly documented with present-day observations despite its primary importance in governing CO₂ sinks. Moreover, we lack precise descriptions of atmospheric processes associated with cloud microphysics and surface-atmosphere exchange in polar regions, and the evolution of westerly wind locations and strength (Fogt and Marshall, 2020).

Over the previous years, we have installed 3 water vapor analyzers on Reunion Island at the Maïdo observatory (21.079°S, 55.383°E, 2160m) (Guilpart et al., 2017) and in Antarctica (Dumont d’Urville and Concordia; (Leroy-Dos Santos et al., 2021; Bréant et al., 2019; Casado et al., 2016) These instruments have been used for the following purposes. They document the diurnal variability of the isotopic signal with the influence of the subtropical westerly jet on the water isotopic signal at night as well as the cyclonic activity in La Réunion. In Antarctica, the
instruments have shown a strong influence of katabatic winds on the isotopic composition of the water vapor (Béant et al., 2019). In order to complete the picture of the atmospheric water cycle over the Indian basin of the Southern Ocean already documented by these three analyzers, we installed a new water vapor isotopic analyzer in the mid-latitude of the south Indian Ocean on Amsterdam Island in November 2019.

The objective of this study is to provide the first analyses of isotopic records (vapor and precipitation) in Amsterdam Island, with a comparison of meteorological data and environmental data collected in parallel on the Amsterdam Island Observatory (e.g. atmospheric mercury) to help interpretation of isotopic records. This study includes analyses of meteorological maps, back trajectories as well as outputs from general circulation models equipped with water isotopes. After a description of the different records over the years 2020 and 2021, model simulations and back trajectory methodology, we focus on some low-pressure events (cold fronts) associated with a strong negative excursion of the $\delta^{18}O$ of water vapor over a few days. These events, expressed strongly in the water vapor isotopic record, are then used for evaluation of general circulation models equipped with water isotopes.

2. Methods

2.1 Site

Labelled a GAW WMO (Global Atmosphere Watch World Meteorological Organization) global site, Amsterdam Island ($37.7983^\circ$ S, $77.5378^\circ$ E) is a remote and very small island of 55 km$^2$ with a population of about 30 residents, located in the southern Indian Ocean at 3300 km and 4200 km downwind from the nearest lands, Madagascar and South Africa, respectively (Sprovieri et al., 2016). Climate is temperate, generally mild with frequent presence of clouds. Seasonal boundaries were defined as follows: winter from July to September and summer from December to February, in line with previous studies (Sciare et al., 2009). Average temperature is lower in winter compared to summer ($10^\circ$C vs $15^\circ$C) while relative humidity and wind speed remain high (respectively 50-85% and 5 to 15 m s$^{-1}$) most of the year without a clear seasonal cycle.

Numerous atmospheric compounds and meteorological parameters are and were continuously monitored at the site from 1960 (Gaudry et al., 1983; Polian et al., 1986; Gros et al., 1999, 1998; Sciare et al., 2000, 2009; Angot et al., 2014; Slemr et al., 2015; El Yazidi et al., 2018; Slemr et al., 2020). In particular, the Amsterdam (AMS) site hosts several dedicated atmospheric observation instruments notably at the Pointe Bénédicte atmospheric observatory (70 m above
sea level) where greenhouse gases (GES) concentration and mercury (Hg) species are monitored (service ICOS-France Atmosphère, ICOS-AMS-416 IPEV program, GMOStral-1028 IPEV program). Both GES and Hg species measurements respond to international monitoring networks (ICOS – https://www.icos-cp.eu/, GEO-GOS4M – http://www.gos4m.org/ for GES and Hg species respectively). CO₂, CO, CH₄ and Hg species have been continuously measured since 1980, 2014, and 2012 respectively.

Figure 1: Location (left) and picture (right) of the Amsterdam Island. CRO: Crozet Island; RUN: La Réunion island; KER: Kerguelen Island; AMS: Amsterdam Island. Picture credit: left – Magand adapted from (Angot et al., 2016); right – Magand

2.2 Long term measurements

2.2.1 Meteorological measurements

Two meteorological stations are installed at the top of an observation mast (25 m above ground level, agl) at the Pointe Bénédicte observatory (data used during this study), since 1980. Installed and managed by ICOS-AMS-416 IPEV program, wind speed and direction, atmospheric pressure, surface temperature and relative humidity are currently measured by a WXT520 Vaisala weather system. Data (minute acquisition frequency) are cleaned and processed by the IGE in the framework of the GMOStral-1028 IPEV program. Another meteorological station is based on the island and is operated by Météo France at Martin-de-Viviers life base around 27 m above sea level, about two kilometers east from the Pointe Bénédicte observatory. This second weather station collects air temperature, humidity,
precipitation, wind speed and direction, pressure and solar radiation via a mercury SYNOP automatic weather station from STERELA meteo company. Only daily precipitation data provided by Meteo France are used in the current study.

2.2.2 Gaseous elemental mercury (GEM)

Atmospheric GEM (Gaseous Elemental Mercury) measurements are conducted since 2012 in the framework of IPEV GMOSstral-1028 observatory program at the Pointe Benedicte atmospheric research facility. Data are freely available on the national GMOS-FR data platform AERIS ((Magand and Dommergue, 2022)) (https://gmos.aeris-data.fr, last access: 07/12/2022). GEM is continuously measured (15 nm data frequency acquisition) using a Tekran 2537 A/B instrument models (Tekran Inc., Toronto, Canada) (Angot et al., 2014; Slemr et al., 2015, 2020; Sprovieri et al., 2016; Li et al., 2023). The operation device is based on mercury enrichment on a gold cartridge, followed by a thermal desorption and a detection by cold vapor atomic fluorescence spectroscopy (CVAFS) at 253.7 nm (Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988). Switching between two cartridges allows for alternating sampling and desorption and thus results in a quasi-continuous temporal coverage of the mercury measurement since the last decade. Concentrations are expressed in nanograms per cubic meters at STP conditions (173.15 K and 1013.25 hPa) with an instrumental detection limit below 0.1 ng m$^{-3}$ and a GEM average uncertainty value around 10% (Slemr et al., 2015). The instrument is automatically calibrated following a strict procedure adapted from that of Dumarey et al. (1985). Ambient air is sampled at 1.2 L min$^{-1}$ through a heated (50°C) and UV protected PTFE sampling line, with an inlet installed outside, 6 m agl. The air is filtered through two 0.45 μm pore size polyether sulphone (PES) and one PTFE 47 mm diameter filters before entering in the Tekran to prevent the introduction of any particulate material into the detection system as well as capture any GOM (Gaseous Oxidised Mercury) or particulate bound mercury (PBM) species ensuring that only GEM is sampled. To ensure the comparability of Hg measurements around the world, the instrument is operated according to the Global Mercury Observation System (GMOS) and CAMNET, AMNET standard operating procedures (Steffen et al., 2012; Sprovieri et al., 2016). The detailed quality assurance and quality control required by GMOS to produce qualified dataset are described in detail in the GMOS-FR data products section in GMOS-FR website data portal (https://gmos.aeris-data.fr last access: 07/12/2022).

In this study, atmospheric GEM is used as potential tracer of intrusion and/or subsidence of high altitude air masses (lower/ upper troposphere, or even above) that may possibly impact the
atmospheric records in Pointe Benedicte Observatory which collects marine boundary layer most of the time (Angot et al., 2014; Sprovieri et al., 2016; Slmer et al., 2015, 2020). As mentioned above, mercury in the atmosphere is detected in three defined forms: GEM, GOM (HgO, HgCl₂, HgBr₂, Hg[OH]₂) and PBM. GEM, the dominant form of atmospheric mercury species, is ubiquitous in the atmospheric reservoir and originates from a multitude of anthropogenic and natural sources (Gaffney et al., 2014; Gworek et al., 2020; Gustin et al., 2020; Edwards et al., 2021). Near the surface (marine or terrestrial boundary layer) and out of polar regions, GOM and PBM represent only a few percent of the total atmospheric mercury (Swartzendruber et al., 2006; Gustin and Jaffe, 2010; Gustin et al., 2015). Even if chemical cycling and spatiotemporal distribution of mercury in the air, whatever atmospheric layer considered (surface, mixed or free troposphere, stratosphere), is still poorly understood and complete GEM oxidation schemes remain still unclear (Shah et al., 2021 and associated references), several studies provided evidence that vertical distribution of atmospheric mercury measurements from boundary layer to lower/upper troposphere and stratosphere shows a decreasing trend in GEM concentration with increasing altitude, in parallel with an increase in the concentration of divalent mercury (GOM + PBM) resulting from GEM oxidation mechanisms (Murphy et al., 2006; Swartzendruber et al., 2006, 2008; Talbot et al., 2007; Fain et al., 2009; Sheu et al., 2010; Lyman and Jaffe, 2012; Brooks et al., 2014; Fu et al., 2016; Koenig et al., 2023). The identification of such observational processes (lower GEM concentrations in high-altitude air masses versus marine boundary layer ones) is used here to help characterizing possible high altitude air masses excursion in low altitude Pointe Benedicte Observatory.

2.3 Water vapor isotopic measurements

The isotopic composition of near-surface water vapor (δ¹⁸O, and δD, in ‰ versus SMOW) and the water vapor mixing ratio (q, in ppmv) have been measured continuously since November 2019. The measurements have been done with a Picarro Inc. instrument (L2130-I model) based on wavelength-scanned cavity ring down spectroscopy. The instrument has been installed in a temperature-controlled room at the observatory on the Amsterdam Island and the sampling of water vapor is done outside at ~ 6 m above ground level.
Figure 2: Dependency of $\delta^D$ (top) and $\delta^{18}O$ (bottom) (anomaly from the true value of the standard) on the mixing ratio. The results are shown for two different standards (GREEN_AMS in green and EPB_AMS in black). The crosses indicate the data obtained with the set-up and the solid lines are the best regression curves (same curves for $\delta^{18}O$ for both standards).

The calibration of the data is performed in different steps following previous studies (Tremoy et al., 2011; Leroy-Dos Santos et al., 2020). First, we quantified the influence of water vapor mixing ratio on the water isotope ratios. This effect is large at very low humidity (Leroy-Dos Santos et al., 2021). It can also depend on the isotopic composition of the standard water (Weng et al., 2020). Here, we introduced two different water standards, EPB-AMS and GREEN-AMS, with respective values of (-5.66 ‰, -47.31 ‰) and (-32.65 ‰, -263.76 ‰) for the couple ($\delta^{18}O$, $\delta^D$) which encompass the isotopic values on site observations. The $\delta^{18}O$ measurements of both EPB-AMS and GREEN-AMS standards decrease with increasing humidity with the same amplitude. In contrast, the $\delta^D$ measurements of both EPB-AMS and GREEN-AMS standards exhibit different behavior: $\delta^D$ of EPB-AMS increases by 1.5‰ and $\delta^D$ of GREEN-AMS decreases by 2.5 ‰ over the same 6,000-24,000 ppmv range for mixing ratio $q_v$.

As a consequence, the raw $\delta^{18}O_v$ measurements are corrected with the following regression:

$$\delta^{18}O_{v,corr} = \delta^{18}O_{v,measured} + 1.1 \times 10^{-5} \times q_v + 0.232$$

(eq 4)
For the correction of the raw $\delta D_v$, we use two different regression splines for EPB-AMS and GREEN-AMS (cf Figure 2):

$$\delta D_{EPB-AMS,corr} = \delta D_{EPB-AMS,measured} + \frac{9300}{q} - 0.383$$  \hspace{1cm} (eq 5)

$$\delta D_{GREEN-AMS,corr} = \delta D_{GREEN-AMS,measured} - \frac{22400}{q} + 1.05$$  \hspace{1cm} (eq 6)

The raw $\delta D_v$ are thus weighted-corrected according to their distance of the measured $\delta D$ value from the EPB_AMS and the GREEN_AMS as follows:

$$\delta D_{c,corr} = \delta D_{GREEN-AMS,corr} + \frac{\delta D_{measured} - \delta D_{GREEN-AMS,measured}}{\delta D_{EPB-AMS,measured} - \delta D_{GREEN-AMS,measured}} \times (\delta D_{EPB-AMS,corr} - \delta D_{GREEN-AMS,corr})$$  \hspace{1cm} (eq 7)

The second calibration step consists in the injection of the same two isotopic standards every 47 h at a mixing ratio of 13,000 ppmv to correct for any long-term drift. The correction associated with this drift is less than 0.4 ‰ for $\delta^{18}O$ and 2.5 ‰ for $\delta D$ over the two years of measurements.

Precipitation were also sampled on a weekly basis in a rain gauge filled with paraffin oil which permits to have measurements of water isotopic composition in the precipitation on a weekly basis. The water samples are then sent for analyses at LSCE and measured on an isotopic analyzer L2130-I by Picarro. The uncertainty associated with this series of measurements is of ±0.15 ‰ for $\delta^{18}O$ and ±0.7 ‰ for $\delta D$ leading to a quadratic error of ±1.4 ‰ for d-excess.

### 2.4 Back trajectories: FLEXPART

The origin and trajectory of air masses were assessed by FLEXPART, which is a Lagrangian particle dispersion model (Pisso et al., 2019). All the meteorological data used to simulate the back trajectories are taken from the ERA5 atmospheric reanalysis (Hersbach et al., 2020) with a 6-hourly resolution. The ERA5 reanalysis is carried out by the European Center for Medium-Range Weather Forecasts (ECMWF), using ECMWF’s Earth System model IFS (Integrated Forecasting System), cycle 41r2. For a few selected events, FLEXPART calculated...
back trajectories over 10 days with 1000 launches of neutral particles (sensitivity test) of inert
air tracers released randomly (volume of 0.1°×0.1°×100 m) every 3 hours at 100 m altitude
above sea level (Leroy-Dos Santos et al., 2020), centered around the coordinates of Amsterdam
Island. The results of FLEXPART back trajectories are then displayed in particle density
probability.

2.5 General atmospheric circulation model equipped with water stable isotopes

2.5.1 LMDZ-is0 model

LMDZ-is0 (Risi et al., 2010) is the isotopic version of the atmospheric general circulation
model LMDZ6 (Hourdin et al., 2020). We have used LMDZ-is0 version 20230111.trunk with
the physical package NPv6.1, identical as the atmospheric setup of IPSL-CM6A (Boucher et
al., 2020) used for phase 6 of the Coupled Model Intercomparison Project (CMIP6, (Eyring et
al., 2016)). We performed two simulations, one at very low horizontal resolution (VLR, 3.75°
in longitude and 1.9° in latitude, 96×95 grid cells) and the second at low horizontal resolution
(LR, 2.0° in longitude and 1.67° in latitude, 144×142 grid cells). Both simulations have 79
vertical levels and the first atmospheric level is located around 10 m above ground level. The
LMDZ-is0 3D-fields of temperature and wind are nudged toward the 6-hourly ERA5 reanalysis
data with a relaxation time of 3 hours. Surface ocean surface boundary conditions are taken
from the monthly mean SST and sea-ice fields from the CMIP6 AMIP Sea Surface Temperature
and Sea Ice dataset version 1.1.8 (Durack et al., 2022; Taylor et al., 2000). LMDZ-is0 outputs
are used at a 3-hourly resolution. The Amsterdam Island (58 km²) is too small to be represented
in the LMDZ-is0 model.

2.5.2 ECHAM6-wiso model

ECHAM6-wiso (Cauquoin et al., 2019; Cauquoin and Werner, 2021) is the isotopic version of
the atmospheric general circulation model ECHAM6 (Stevens et al., 2013). The
implementation of the water isotopes in ECHAM6 has been described in detail by Cauquoin et
al. (2019), and has been updated in several aspects by Cauquoin and Werner (2021) to make
the model results more consistent with the last findings based on water isotope observations
isotopic composition of snow on sea ice considered, supersaturation equation slightly updated, and kinetic fractionation factors for oceanic evaporation assumed as independent of wind speed. We have used ECHAM6-wiso model outputs from a simulation at T127L95 high spatial resolution (0.9° horizontal resolution and 95 vertical levels) nudged to ERA5 reanalysis (Hersbach et al., 2020). ECHAM6-wiso is thus run with a finer resolution than both LMDZ-iso simulations. The ECHAM6-wiso 3D-fields of temperature, vorticity and divergence as well as the surface pressure field were nudged toward the ERA5 reanalysis data every 6 hours. The orbital parameters and greenhouse gases concentrations have been set to the values of the corresponding model year. The monthly mean sea surface temperature and sea-ice fields from the ERA5 reanalysis have been applied as ocean surface boundary conditions, as well as a mean δ¹⁸O of surface seawater reconstruction from the global gridded data set of (LeGrande and Schmidt, 2006). As no equivalent data set of the δD composition of seawater exists, the δD of the seawater in any grid cell has been set equal to the related δ¹⁸O composition, multiplied by a factor of 8, in accordance with the observed relation for meteoric water on a global scale (Craig, 1961). The ECHAM6-wiso simulation is described in detail and evaluated in Cauquoin and Werner (2021). ECHAM6-wiso outputs are given at a 6-hourly resolution. As for the LMDZ-iso model, the Amsterdam Island (58 km²) is too small to be represented by ECHAM6-wiso.
3. Results

3.1 Data description

Figure 3: Meteorological, isotopic and GEM records for the years 2020 and 2021 on the Amsterdam Island: (a) correlation coefficient between water vapor $\delta^{18}O$ and mixing ratio (dark blue, top) and between water vapor $\delta^{18}O$ and d-excess (light blue, bottom) over a moving time window of 8 days, (b) atmospheric pressure (hourly average), (c) atmospheric temperature (hourly average), (d) mixing ratio (hourly average), (e) $\delta^{18}O$ of water vapor (hourly average), (f) d-excess of water vapor (hourly average), (g) $\delta^{18}O$ of precipitation sampled on a weekly basis, (h) GEM concentration, (i) daily precipitation. The green rectangles indicate the period with (1) correlation coefficient $>-0.5$ between d-excess and $\delta^{18}O$ of water vapor and (2) occurrence of a negative excursion in water vapor $\delta^{18}O$. 

https://doi.org/10.5194/egusphere-2023-1617 
Preprint. Discussion started: 22 August 2023 
© Author(s) 2023. CC BY 4.0 License.
3.1.1 Temporal variability in the meteorological records

As mentioned earlier, there is a clear annual cycle at Amsterdam Island as recorded in the temperature and water mixing ratio for the years 2020 and 2021. The December-February period (austral summer) has the highest temperatures with an average of 15.0°C, while in winter (July-September) the average temperature varies around 10.5°C. In parallel, we do not see clear patterns of a diurnal cycle except for some periods in the temperature records yet with a small amplitude (4-5 °C).

The impact of synoptic events at the scale of a few days is visible in the temperature and water mixing ratio with a covariation of temperature and water mixing ratio with amplitude of up to 10°C in temperature and more than 10,000 ppmv in water mixing ratio.

3.1.2 Temporal variability in the GEM record

Previous studies clearly showed that AMS is little influenced by anthropogenic sources of Hg, and greatly influenced by the ocean surrounding the island (Angot et al., 2014; Slemr et al., 2015, 2020; Jiskra et al., 2018; Li et al., 2023; Hoang et al., 2023). Angot et al., (2014) reported mean annual GEM concentrations of about 1.03 ± 0.08 ng m⁻³ from 2012 to 2013. These concentrations are ~30% lower than those measured in remote sites of the northern hemisphere.

Over the period 2012 to 2017, Slemr et al. (2020) confirmed that higher GEM concentrations can be found during austral winter. Lower GEM values are generally observed in October and November, as well as in January and February during austral summer. Using this 6-yr long data set, mean annual GEM concentration was 1.04 ± 0.07 ng m⁻³ (annual range: 1.014 to 1.080 ng m⁻³) i.e. very close to the one observed in Angot et al (2014).

During the period (2020-2021) of water vapor isotope measurements in AMS, GEM showed mean annual concentration in the range of 1.11 ± 0.04 ng m⁻³ and 1.00 ± 0.04 ng m⁻³, for years 2020 and 2021 respectively, slightly higher and lower than the ones observed in previous mentioned studies. Surprisingly, unlike the 2012-2017 data set, GEM presented in this study did not show a significant higher mean concentration during the austral winter months than during the summer months (Figure 3), with consequently no discernible seasonal amplitude of GEM. On a finer timescale, the lack of a clear pattern of GEM seasonal cycle is counterbalanced by days showing abrupt increases or decreases in concentrations. Some of the sudden GEM decreases (until more than 15 % of the concentration in few hours, i.e. up to 0.15-0.20 ng m⁻³ difference) appear concomitant with important negative peak of several ‰ in water vapor δ¹⁸O.

3.1.3 Temporal variability of water isotopic composition
The isotopic composition of precipitation (δ¹⁸Op) sampled on a weekly basis displays a quite large variability (δ¹⁸Op = -3.06 ± 1.75 ‰, n=104) with values slightly higher during austral summer (difference between summer and winter δ¹⁸Op values is about 2 to 3 ‰) (Figure 3). No significant seasonal variations are observed in the record of d-excess of the precipitation. No diurnal cycle can be detected in the δ¹⁸Ov and d-excess. The annual cycles are also not visible (1 ‰ difference between summer and winter mean δ¹⁸Ov value while standard deviation of the entire record at 1 h resolution is 1.7 ‰). Only the synoptic scale variability is well expressed in the records of δ¹⁸Ov and d-excess, with an anticorrelation between both parameters when looking at the 2-year series at hourly resolution (R² = 0.61). Moreover, water vapor δ¹⁸O is most of the time correlated with water mixing ratio (R² = 0.55 for the 2-year series at hourly resolution).

There are a few exceptions to the general correlation between water vapor δ¹⁸O and mixing ratio as illustrated on Figure 3. Short periods of a few days are associated with a decrease of the correlation coefficient, R, between δ¹⁸Ov and qv (R is calculated continuously from hourly records in 8 consecutive days). The periods of decreased R are also characterized by a negative peak of several ‰ in δ¹⁸Ov, which are not visible in the d-excess. During these δ¹⁸Ov excursions occurring during cold fronts, the general anti-correlation between δ¹⁸Ov and d-excess, hence also breaks down. Our study mostly focuses on the 11 abrupt events highlighted by the water vapor δ¹⁸O record (only 10 visible on Figure 3 because of the scale).

### 3.2 Model-data comparison
Figure 4: Data model comparison (January – March 2020): water vapor $\delta^{18}$O from our data set (light blue on hourly average, dark blue resampled at a 6-hour resolution), the ECHAM6-wiso model (green, surface level, 6h resolution) and the LMDZ-iso model (red, surface level, 3h resolution) at very low resolution (VLR, dashed line) and at low resolution (LR, solid line) (a); mixing ratio from our data set (light blue on hourly average, dark blue resampled at a 6 hours resolution), the ECHAM6-wiso model (green, surface level, 6h resolution) and the LMDZ-iso model (red, surface level, 3h resolution, dashed line for VLR and solid line for LR) (b); vertical velocity from the ERA5 reanalyses (500 hPa, blue, 850 hPa, light blue), from the ECHAM6-wiso model (500 hPa, green, 850 hPa, light green), from the LMDZ-iso model at LR (500 hPa, red, 850 hPa, orange) (c); Precipitation amount from the meteorological record in light blue, from the ECHAM6-wiso model in green and from the LMDZ-iso model in red (dashed line VLR and solid line LR) (d). The grey rectangles highlight the negative $\delta^{18}$O excursions (note that in this figure the excursions of the 3rd and 9th of January 2020 are distinct while the distinction could not be done on Figure 3 because of the scale).

We selected a 3-month period (January to March 2020) for the comparison between our set of data and the outputs of the ECHAM6-wiso and LMDZ-iso models. This period has been selected for display because it encompasses 4 out the 11 negative excursions of $\delta^{18}$O, but the extended comparison over the whole 2 years period is displayed on Figure S1. There is an overall agreement between the measured and modelled water vapor $\delta^{18}$O and mixing ratio (Figure 4). The best agreement over the 3-month series is obtained with the ECHAM6-wiso and LMDZ-iso (LR) models ($R^2 = 0.59 - 0.6$ and $0.87 - 0.90$ respectively for $\delta^{18}$O and mixing ratio series) while a slightly less good agreement is observed with the VLR simulation of the LMDZ-iso model ($R^2 = 0.49$ and 0.79 respectively for $\delta^{18}$O and mixing ratio series). The same observation can be done on the entire two-year series. We also compare the precipitation amount modelled by ECHAM6-wiso and LMDZ-iso to the precipitation amount measured by the MeteoFrance weather station and in general, the agreement with measured precipitation amount is better for ECHAM6-wiso ($R^2 = 0.45$) than for LMDZ-iso ($R^2 = 0.08 - 0.13$ for VLR - LR). Finally, when focusing on the 4 short term negative excursions of the water vapor $\delta^{18}$O (grey rectangles in Figure 5), they are in general more strongly expressed in the data series than in the model series which is only partly due to the hourly resolution of the $\delta^{18}$O record compared to the 3h and 6h resolution of the outputs of the LMDZ-iso and ECHAM6-wiso models respectively (Figure 4 red dashed and solid lines on panel c and Table 1 9th column).
When looking at the whole two-year series, the LMDZ-iso VLR simulation fails to reproduce most of these excursions (only the negative excursion of the 3rd of January 2020 is reproduced) while the ECHAM6-wiso model is able to capture all the excursions. The LMDZ-iso LR simulation produces a negative $\delta^{18}$Ov excursion over many events but significantly less expressed than in the data and in the ECHAM6-wiso model (Table 1).

4. Discussion

The most remarkable pattern from this two-year series is the succession of short negative excursions of $\delta^{18}$O, associated with decorrelation between $\delta^{18}$Ov and humidity, $\delta^{18}$Ov and d-excess, and highlighted with green rectangles in Figure 3 and referenced in Table 1. They always occurred during low pressure periods (atmospheric pressure below 1005 mbar). The focus on the first three months of the series presented on Figure 4 shows that these events are captured by ECHAM-wiso at 0.9° resolution, but not systematically by LMDZ-iso at 2x1.67° and even less by LMDZ-iso at 3.75x1.9° resolution. Such mismatch makes the understanding of the processes at play during these events particularly important to test and improve the performances of atmospheric general circulation models equipped with water isotopes.

**Figure 5**: Evolution of GEM, water vapor $\delta^{18}$O, mixing ratio, meteorological parameters (surface temperature, surface atmospheric pressure, daily precipitation) measured by the MeteoFrance weather station and vertical velocity from the ERA5 reanalyses at 500 and 850 hPa over the three isotopic excursions of January 2020 identified on Figure 4.
Table 1: List of the cold front events associated with both loss of correlation between δ¹⁸Ov and qv, δ¹⁸Ov and d-excess, and negative excursions of δ¹⁸Ov over 2020-2021. The length of the event is estimated from the time difference between the mid slope of the δ¹⁸Ov decrease at the beginning of the event and the mid-slope of the δ¹⁸Ov increase at the end of the event. The amplitude of the negative δ¹⁸Ov anomaly is calculated between the average δ¹⁸Ov level 24h before and 24h after the excursion and the minimum of δ¹⁸Ov on the record at hourly resolution (at 6h resolution). When the calculated amplitude is smaller than 1‰, we indicate only “~”.

When the vertical velocity is between -0.25 and 0.25 Pa/s, we indicate “~0”.

<table>
<thead>
<tr>
<th>Date of the event</th>
<th>Negative excursion of GEM</th>
<th>Low pressure (&lt;1005 mbar)</th>
<th>Rain</th>
<th>Relative Humidity at the surface</th>
<th>vertical velocity from reanalyses (850 hPa)</th>
<th>vertical velocity from reanalyses (500 hPa)</th>
<th>Length of the event (hours)</th>
<th>amplitude of the δ¹⁸O peak in the data (‰)</th>
<th>amplitude of the δ¹⁸O peak in ECHAM-wiso (‰)</th>
<th>amplitude of the δ¹⁸O peak in LMDZ-iso VLR (‰)</th>
<th>amplitude of the δ¹⁸O peak in LMDZ-iso LR (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/12/2021</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>82%</td>
<td>~0</td>
<td>up</td>
<td>3h</td>
<td>-6 (-5)</td>
<td>-2.3</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>08/11/2021</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>85%</td>
<td>~0</td>
<td>~0</td>
<td>17h</td>
<td>-5.5 (-5.5)</td>
<td>-5</td>
<td>-4</td>
<td>-4</td>
</tr>
<tr>
<td>23/06/2021</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>75%</td>
<td>~0</td>
<td>~0</td>
<td>10h</td>
<td>-5.5 (-5.4)</td>
<td>-6</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>07/06/2021</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>80%</td>
<td>up</td>
<td>~0</td>
<td>9h</td>
<td>-6.5 (-5.8)</td>
<td>-5.8</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>08/03/2021</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>89%</td>
<td>down</td>
<td>up</td>
<td>20h</td>
<td>-6 (-4)</td>
<td>-4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>09/08/2020</td>
<td>No data</td>
<td>Yes</td>
<td>Yes</td>
<td>87%</td>
<td>down</td>
<td>up</td>
<td>8h</td>
<td>-8 (-6)</td>
<td>-7</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>10/05/2020</td>
<td>Small</td>
<td>Yes</td>
<td>Yes</td>
<td>95%</td>
<td>down</td>
<td>down</td>
<td>14h</td>
<td>-4.9 (-4)</td>
<td>-3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>04/03/2020</td>
<td>No data</td>
<td>Yes</td>
<td>Yes</td>
<td>98%</td>
<td>Up</td>
<td>Up</td>
<td>9h</td>
<td>-6.1 (-5.3)</td>
<td>-5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24/01/2020</td>
<td>No data</td>
<td>Yes</td>
<td>Yes</td>
<td>93% and 90%</td>
<td>1st peak up and 2nd peak down</td>
<td>1st peak up and 2nd peak down</td>
<td>17h</td>
<td>-7.8 (-7.5)</td>
<td>-4.5</td>
<td>-3.5</td>
<td>-3.5</td>
</tr>
<tr>
<td>09/01/2020</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>94%</td>
<td>up</td>
<td>up</td>
<td>4h</td>
<td>-9 (-4)</td>
<td>-5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>03/01/2020</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>90%</td>
<td>~0</td>
<td>6h</td>
<td>-2.8 (-2.5)</td>
<td>-2.4</td>
<td>-3</td>
<td>-3.5</td>
<td>-3.5</td>
</tr>
</tbody>
</table>

Several hypotheses can be proposed to explain the negative excursions of water vapor δ¹⁸O during cold front periods. The beginning of these excursions is associated with a decrease of water mixing ratio and they occur in most cases (but not always) during a precipitation event (Table 1). These events share similarities with the negative δ¹⁸Ov, δ¹⁸Op short events previously observed in temperate regions during a cold front passage (e.g. Aemisegger et al., 2015). Three possible processes at play to explain such events were already listed in previous studies (e.g. Dütsch et al., 2016) (i) local interaction between the vapor and the rain droplets (rain equilibration and rain evaporation), (ii) vertical subsidence of water vapor with depleted isotopic composition, or (iii) horizontal advection through the arrival of a cold front.
Figure 6: Evolution of the mixing ratio and isotopic composition of water vapor for the different events (colors according to the date as explained on the graph) and for the entire 2 years records (grey). The solid lines are theoretical lines inspired from (Noone, 2012) for different processes (remoistening associated with exchange between rain and water vapor; Rayleigh distillation assuming that all formed condensation is removed from the cloud; moist adiabatic process assuming that liquid condensation stays in the cloud with the water vapor; mixing of water vapor from ocean evaporation around Amsterdam Island and water vapor from the end of the Rayleigh distillation, i.e. high altitude water vapor). The water vapor for the calculation of Rayleigh distillation and for the evaporation above the ocean has a mixing ratio of 20,000 ppmv and a $\delta^{18}O_v$ of -9.3‰. The vapor at the end of the distillation line was taken with a mixing ratio of 1,000 ppmv and a $\delta^{18}O_v$ of -40‰.

We first explore how we can gain information on the different processes listed above from our data set. First, to test the hypothesis of vapor-droplet interactions, we looked at the $\delta^{18}O_v$ vs $q_v$ distribution (Figure 6). In general, the $\delta^{18}O_v$ vs $q_v$ evolution lies on a curve which can be explained by condensation processes (Rayleigh distillation or reversible moist adiabatic process). However, for the 11 events highlighted above, the $\delta^{18}O_v$ vs $q_v$ evolution follows an evolution characteristic of remoistening processes, i.e. a curve standing below the curve of the $\delta^{18}O_v$ vs $q_v$ evolution observed for the rest of the series, which demonstrates the depleting effect.
of vapor-rain interactions (Worden et al., 2007; Noone, 2012). Since relative humidity is relatively high during these events (values given in Table 1 compared to a mean value of 77 %), it more likely reflects rain-vapor diffusive exchanges than rain evaporation.

Second, to test the hypothesis, of subsidence of air from higher altitude, GEM is used. Indeed, aircraft measurements as well as model simulations demonstrated that the upper troposphere/lower stratosphere (UTLS) is depleted in GEM and enriched in species composed of reactive gaseous mercury and particulate bound mercury (Murphy et al., 2006; Swartendruber et al., 2006, 2008; Sillman et al., 2007; Talbot et al., 2007, 2008; Lyman and Jaffe, 2012). This leads to lower GEM concentrations than those usually observed when the lowest atmosphere layer is only under marine influence (Lindberg et al., 2007; Angot et al., 2014). The fact that GEM negative excursions are observed in phase with negative δ¹⁸Ov excursions in most of the events (7 events on a total of 9 events with GEM data, cf Figure 5, Table 1) suggests that vertical subsidence of water vapor, δ¹⁸O-depleted by Rayleigh distillation and/or rain-vapor interactions, can have an influence on the observed excursions of δ¹⁸Ov, in agreement with the conclusion of Dütsch et al. (2016).

To further explore the processes leading to the decoupling of humidity and δ¹⁸Ov as well as sharp negative excursions of δ¹⁸O, during the 11 events identified here, we also use information from the ERA5 reanalyses. In particular, the influence of atmospheric circulation (vertical and horizontal advection) can be studied through back trajectories. The back trajectories (see some examples in SI, Figures S2 and S3) confirm the information from wind directions that there is no systematic change in the horizontal origin of the trajectories for the different events. On the contrary, back trajectories clearly indicate a strong subsidence over some events, in particular for the event of the 3rd of January: the maximum altitude of the envelope of the back trajectories increases from 5,000 to 8,000 m when comparing the situation before the excursion and the situation during the most negative water vapor δ¹⁸O value, hence confirming the occurrence of air subsidence indicated by the GEM record (Figure S2). A less clear but similar situation is observed for the anomaly of the 24th of January 2020 which is associated with an increase of the maximum altitude of the back trajectories from 4,000 to 6,000 m when comparing the situation before the excursion and the situation corresponding to the most negative water vapor δ¹⁸O value. Back trajectories are however not supporting systematic subsidence for other cases (e.g. event of the 9th of January, Figure S3).

The subsidence over the different events can also directly be followed on the vertical velocity from the ERA5 reanalyses (Figure 4). Subsidence (positive vertical velocity) is not
systematically associated with negative δ\(^{18}\)O excursions: subsidence at either 850 hPa or 500 hPa is observed only for 5 events over 11 (Table 1). In 4 cases, there is rather an ascending movement of the atmosphere associated with the rain event. In the other cases, there is no clear vertical movement. However, we note that when negative δ\(^{18}\)O excursions are not concomitant with subsidence, they occur right after an ascending movement and are generally followed by subsidence (Figure S1).

The effect of change in horizontal air mass origin is difficult to study from our data. There is no evidence for changes in the horizontal advection of air over the 11 particular events from the observation of wind direction around these cold front events. The back trajectories permit to look at a possible change of horizontal advection higher in the atmosphere. Again, no clear change of horizontal advection at higher altitude is observed for the 11 events associated with a sharp decrease of the δ\(^{18}\)O. With the information gathered above, both subsidence and isotopic depletion associated with rain occurrence and further interaction between droplets and water vapor can explain the negative excursion of δ\(^{18}\)O. We note however that the data gathered so far do not permit to provide a simple and unique explanation. Neither subsidence nor rain systematically occurred for each of the δ\(^{18}\)O excursions. Still, the fact that at least ECHAM6-wiso is able to reproduce every negative δ\(^{18}\)O excursions (whether they are associated or not with subsidence or rain-water vapor reequilibration) shows that the atmospheric circulation patterns are correctly reproduced and that the isotopic processes are correctly implemented in this model. Such abrupt δ\(^{18}\)O excursions can hence be used as a test of the performances of general circulation models equipped with water isotopes.

To better understand why the models are less able to reproduce the δ\(^{18}\)O excursions at coarser resolution, we compare the performances of the ECHAM6-wiso and the LMDZ-iso models over the first months of 2020 in term of atmospheric dynamic (the whole series is displayed in SOM). First, the two models reproduce rather well the evolution of the vertical velocity from the ERA5 reanalyses with a stronger ascent for the model predicting the strongest precipitation amount (e.g. LMDZ-iso for 24\(^{th}\) of January 2020). The event of the 3\(^{rd}\) of January is the only one reproduced by both ECHAM6-wiso and the two versions of the LMDZ-iso model: the three simulations show a clear subsidence over the isotopic event and a clear negative δ\(^{18}\)O excursion (Figure 4). For the other events, neither LMDZ-iso nor ECHAM6-wiso show a clear signal of subsidence neither at 500 nor at 850 hPa (Figure 4). However, the horizontal distribution of vertical velocity obtained with ECHAM6-wiso and LMDZ-iso are significantly different
(Figure 7 for the event of the 9th of January, Figures S5 for the other events). While the LMDZ-
iso modelled vertical velocity displays a rather strong homogeneity on the vertical axis,
ECHAM6-wiso modelled vertical velocity highlights subsidence of air below the ascending
column at the exact location of the negative δ¹⁸Ov anomaly (Figure 7c). This subsidence of
depleted δ¹⁸Ov below the ascending column is responsible for the sharp negative δ¹⁸Ov
excursion in the ECHAM6-wiso model. The fact that subsidence of air occurs just below
uplifted air, at the limit between ascendance and subsidence (Figure 7j), permits to reconcile
the GEM data suggesting subsidence and the sign of the vertical velocity of the ERA5
reanalyses at Amsterdam Island. We propose that the reason why the LMDZ-iso model does
not reproduce well the water isotopic anomaly is its too coarse resolution. Indeed, Table 1 and
Figure 4 show that for the event of the 24th of January, the LMDZ-iso model at low resolution
is able to reproduce the isotopic anomaly while the LMDZ-iso model at very low resolution
fails. A fine resolution is necessary to capture the details of the spatial patterns of the vertical
velocity and ¹⁸O. Similar observations can be done on other events as shown in the SI (Figures
S5 to S11).

Figure 8 summarizes the proposed mechanism for negative δ¹⁸O, excursions as inferred from
our data – model comparison when there is a clear rain event. A rain event is associated with a
strong ascending column in which δ¹⁸Ov is depleted by progressive precipitation during the
ascent and by interaction between rain and water vapor. This ascending column is coupled to
the subsidence of δ¹⁸Ov, depleted air at the rear of the event which is pushed toward Amsterdam
Island through a south west advection of cold air.
Figure 7: Evolution of the modelled $\delta^{18}$Ov and vertical velocity over the event of the 9th of January 2020. (a) low level (~83 m) contourplot of $\delta^{18}$O, on a latitude vs longitude plot, the yellow line indicates the -15‰ level and grey contours indicate precipitation contours at 0.5, 10, and 50 mm day$^{-1}$ (thin, medium and thick lines respectively); (b) $\delta^{18}$Ov evolution on a altitude vs longitude plot, the yellow lines indicate the $\delta^{18}$Ov levels at -30 and -15 ‰, the blue plot the contour of ~0.05 Pa s$^{-1}$ vertical velocity (ascendance) and the vertical black line denotes Amsterdam Island latitude; (c) vertical velocity evolution on an altitude vs longitude plot with similar lines as in (b) ; (a), (b) and (c) are drawn using outputs of the ECHAM6-wiso model ; (d), (e) and (f) are the same as (a), (b) and (c) but obtained from the LMDZ-iso model at low resolution (LR) ; (g), (h) and (i) are the same as (a), (b) and (c) but obtained from the LMDZ-iso model at very low resolution (VLR); (j) shows the vertical velocity on a altitude vs longitude plot from ERA5.
Figure 8: Scheme of the mechanism explaining the sharp negative excursion of $\delta^{18}O_v$ recorded at the surface for cold front events associated with precipitation. The top panel shows the altitude vs longitude dynamics of air masses with vertical saturated lifting in the center and subsidence at the rear of the lifting. The bottom panel shows the associated evolution of $\delta^{18}O_v$ and precipitations on the same longitude scale than on the upper panel.

5. Conclusion

We presented here the first water vapor isotopic record over 2 years in Amsterdam Island. The water vapor isotopic variations follow at first order the variations of water mixing ratio as expected from a marine site. Superimposed to this variability, we have evidenced 11 periods of a few hours / days where the correlation between $\delta^{18}O_v$ and water mixing does not hold. These periods are associated with the occurrence of one or two abrupt negative excursions of $\delta^{18}O_v$. These negative excursions associated with cold fronts are often occurring toward the end of
precipitation events. They are characterized by a decrease in water mixing ratio. Representation of these short events is a challenge for the atmospheric components of Earth System Models equipped with water isotopes and we found that the ECHAM6-wiso model was able to reproduce most of the sharp negative δ18O excursions while the LMDZ-iso model at 2° (3°) resolution was only able to reproduce 7 (1) of the negative excursions.

Using previous modeling studies as well as information provided by (1) confrontation with other data sources (GEM, meteorology) obtained in parallel on this site, (2) back trajectory analyses and (3) the outputs of the two models ECHAM6-wiso and LMDZ-iso, we conclude that the most plausible explanations for such events are rain-vapor interactions and subsidence at the rear of a precipitation event. Both can be combined, since rain vapor interactions can help maintain moist conditions in subsidence regions.

This study highlighted the added value of combining different data from an atmospheric observatory to understand the dynamic of the atmospheric circulation. The two-year records are also a good benchmark for model evaluation. We have especially shown that the isotopic composition of water vapor is a powerful tool to identify aspects to be improved in the general circulation models, such as the horizontal resolution which may influence the representativity of the vertical dynamics.

Data availability: AMS L2 GEM data (https://doi.org/10.25326/168) are freely available (Magand and Dommergue, 2021) at https://gmos.aeris-data.fr/ from national GMOS-FR website data portal coordinated by IGE (Institut des Géosciences de l’Environnement, Grenoble, France; technical PI: Olivier Magand) with the support of the French national AERIS-SEDOO partners, data and services center for the atmosphere (last access: 08 December 2022). Water isotopic data and modeling outputs are available on the Zenodo platform (https://zenodo.org/record/8164392; https://zenodo.org/record/8160871).

Acknowledgements: We deeply thank all overwintering staff at AMS and the French Polar Institute Paul-Emile Victor (IPEV) staff and scientists who helped with the setup and maintenance of the experiment at AMS in the framework of the GMOSTral-1028 IPEV program, the ICOS-416 program and the ADELISE-1205 IPEV program. Amsterdam Island Hg0 data, accessible in national GMOS-FR website data portal (https://gmos.aeris-data.fr/) were collected via instruments coordinated by the IGE-PTICHA technical platform dedicated to atmospheric chemistry field instrumentation. GMOS-FR data portal is maintained by the French national center for Atmospheric data and services AERIS, which is acknowledged by
the authors. The LMDZ-iso simulation were performed thanks to granted access to the HPC resources of IDRIS under the allocations 2022-AD010114000 and 2022-AD010107632R1 and made by GENCI. We deeply thank Sébastien Nguyen (CEA, LSCE) for his help and support in running LMDZiso simulation.

Funding: This work benefited from the IPSL-CGS EUR and was supported by a grant from the French government under the Programme d'Investissements d'avenir, reference ANR-11-IDEX-0004-17-EURE-0006, managed by the Agence Nationale de la Recherche. This project has also been supported by the LEFE IMAGO project ADELISE. Amsterdam Island GEM data, accessible in national GMOS-FR website data portal (https://gmos.aeris-data.fr/) have been collected with funding from European Union 7th Framework Programme project Global Mercury Observation System (GMOS 2010-2015 Nr. 26511), the French Polar Institute IPEV via GOMStral-1028 IPEV program since 2012, the LEFE CHAT CNRS/INSU (TOPMODEL project, Nr. AO2017-984931) and the H2020 ERA-PLANET (Nr. 689443) iGOSP program. This work is part of the AWACA project that has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant agreement No. 951596). The ERA5 reanalyses files for the ECHAM6-wiso nudging have been provided by the German Climate Computing Center (DKRZ). The ECHAM6-wiso simulations have been performed with support of the Alfred Wegener Institute (AWI) supercomputing centre.

Author contributions: AL designed the study and analyzed the data together with FV, CS, EF, OM. OC installed the water vapor isotopic analyzer in Amsterdam Island and OJ was in charge of the data calibration. BM and FP performed the measurements of the isotopic composition of the precipitation samples. CA analyzed the modeling outputs, realized most of the s and performed model-data analyses. CLDS performed the back trajectory analyses with help from MC. OM, AD and YB provided expertise on GEM analyses and interpretation. AC, CR, ND and MW provided model simulations. AL wrote the paper with contribution of all coauthors.

Competing interests: One of the coauthors (AD) is a member of the editorial board of Atmospheric Chemistry and Physics.
References


Boucher, O., Servonnat, J., Albright, A. L., Aumont, O., Balkanski, Y., Bastrakov, V., Bekki, S., Bonnet, R., Bony, S., Bopp, L., Braconnot, P., Brockmann, P., Cadule, P., Caubel, A., Cheruy, F.,
Codron, F., Cozic, A., Cugnet, D., D’Andrea, F., Davini, P., de Lavergne, C., Denvil, S., Deshayes, J.,
735 S., Foujols, M.-A., Gardoll, S., Gastineau, G., Ghattas, J., Grandpeix, J.-Y., Guenet, B., Guez, E.,
736 Lionel, Guilyardi, E., Guimberteau, M., Hauglustaine, D., Hourdin, F., Idelkadi, A., Joussaume, S.,
737 Kageyama, M., Khodri, M., Krinner, G., Lebas, N., Levavasseur, G., Lévy, C., Li, L., Lott, F., Lurton,
738 T., Luyssebert, S., Madec, G., Madeleine, J.-B., Maignan, F., Marchand, M., Marti, O., Mellul, L.,
739 Meurdesoif, Y., Mignot, J., Musat, I., Ottlé, C., Peylin, P., Planton, Y., Polcher, J., Rio, C., Rochetin,
740 N., Rouset, C., Sepulchre, P., Sima, A., Swingedouw, D., Thébélémont, R., Traore, A. K.,
742 the IPSL-CM6A-LR Climate Model, Journal of Advances in Modeling Earth Systems, 12,
744 Bréant, C., Leroy Dos Santos, C., Agosta, C., Casado, M., Fourré, E., Goursaud, S., Masson-Delmotte,
746 vapor isotopic composition driven by katabatic wind variability in summer at Dumont d’Urville,
747 coastal East Antarctica, Earth and Planetary Science Letters, 514, 37–47,
748 https://doi.org/10.1016/j.epsl.2019.03.004, 2019.
751 Casado, M., Landais, A., Masson-Delmotte, V., Gentonth, C., Kerstel, E., Kassi, S., Arnaud, L., Picard,
752 G., Prié, F., Cattani, O., Steen-Larsen, H.-C., Vignon, E., and Cermak, P.: Continuous measurements
753 of isotopic composition of water vapour on the East Antarctic Plateau, Atmospheric Chemistry and
754 Physics, 16, https://doi.org/10.5194/acp-16-8521-2016, 2016.
755 Cauquoin, A. and Werner, M.: High-Resolution Nudged Isotope Modeling With ECHAM6-Wiso:
756 Impacts of Updated Model and ERA5 Reanalysis Data, Journal of Advances in Modeling
758 Cauquoin, A., Werner, M., and Lohmann, G.: Water isotopes -- climate relationships for the mid-
759 Holocene and preindustrial period simulated with an isotope-enabled version of MPI-ESM, Climate of
761 Craig, H.: Isotopic Variations in Meteoric Waters, Science, 133, 1702–1703,
763 Dahinden, F., Aemisegger, F., Wernli, H., Schneider, M., Diekmann, C. J., Ertl, B., Knippertz, P.,
764 Werner, M., and Pfahl, S.: Disentangling different moisture transport pathways over the eastern
765 subtropical North Atlantic using multi-platform isotope observations and high-resolution numerical
766 modelling, Atmospheric Chemistry and Physics, 21, 16319–16347, https://doi.org/10.5194/acp-21-
770 calibration method for the determination of mercury by amalgamation/cold-vapour atomic absorption
772 Durack, P. J., Taylor, K. E., Ames, S., Po-Chedley, S., and Mauzy, C.: PCMDI AMIP SST and sea-
773 ice boundary conditions version 1.1.8, https://doi.org/10.22033/ESGF/input4MIPs.16921, 2022.
774 Dütsch, M., Pfahl, S., and Wernli, H.: Drivers of δ2H variations in an idealized extratropical cyclone,


Fain, X.; Obrist, D.; Hallar, A. G.; McCubbin, I.; Rahn, T. High levels of reactive gaseous mercury observed at a high elevation research laboratory in the Rocky Mountains. *Atmos. Chem. Phys.* 2009, 9 (20) 8049–8060 DOI: 10.5194/acp-9-8049-2009.


Guilpart, E., Vimeux, F., Evan, S., Brioude, J., Metzger, J., Barthe, C., Risi, C., and Cattani, O.: The isotopic composition of near-surface water vapor at the Maïdo observatory (Reunion Island,
southwestern Indian Ocean) documents the controls of the humidity of the subtropical troposphere,

Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., and Heidecorn, K.: Measuring and modeling

Gustin, M. S., Bank, M. S., Bishop, K., Bowman, K., Brafireun, B., Chételat, J., Eckley, C. S.,
Hammerschmidt, C. R., Lamborg, C., Lyman, S., Martínez-Cortizas, A., Sommar, J., Tsz-Ki Tsui, M.,

Gworek, B., Dmuchowski, W. & Baczewska-Dąbrowska, A.H. Mercury in the terrestrial environment:

Hoang, C., Magand, O., Brioude, J., Dimuro, A., Brunet, C., Ah-Peng, C., Bertrand, Y., Dommergue,
A., Lei, Y. D., and Wania, F.: Probing the limits of sampling gaseous elemental mercury passively in
2023.

Houdini, F., Rio, C., Grandpeix, J.-Y., Madeleine, J.-B., Cheruy, F., Rochetin, N., Jam, A., Musat, I.,
Idelkadi, A., Fairhead, L., Foujols, M.-A., Mellul, L., Traore, A.-K., Dufresne, J.-L., Boucher, O.,
Lefebvre, M.-P., Milour, E., Vignon, E., Jouhaud, J., Diallo, F. B., Lott, F., Gastineau, G., Caubel, A.,
Meurdesoif, Y., and Ghittas, J.: LMDZ6A: The Atmospheric Component of the IPSL Climate Model
With Improved and Better Tuned Physics, Journal of Advances in Modeling Earth Systems, 12,
2020.


Jiskra, M., Sonke, J. E., Obrist, D., Bieser, J., Ebinghaus, R., Myhre, C. L., Pfaffhuber, K. A.,
Wängberg, I., Kylloinen, K., Worthy, D., Martin, L. G., Labuschagne, C., Mkololo, T., Ramonet, M.,
Magand, O., and Dommergue, A.: A vegetation control on seasonal variations in global atmospheric
mercury concentrations, Nature Geoscience, 11, 244–250, https://doi.org/10.1038/s41561-018-0078-8,
2018.

Koenning, A.M., Magand, O., Verreyken, B., Brioude, J., Amelynck, C., Schoon, N., Colomb, A.,
troposphere and bidirectional atmosphere-vegetation exchanges – Insights from Maido observatory in
the southern hemisphere tropics. Atmos. Chem. Phys., 23, 1309-1328, https://doi.org/10.5194/acp-23-
1309-2023.

stable water isotope signals from convective and large-scale precipitation phases of a heavy
precipitation event in southern Italy during HyMeX IOP 13: a modelling perspective, Atmospheric
Chemistry and Physics, 19, 7487–7506, 2019.

LeGrande, A. N. and Schmidt, G. A.: Global gridded data set of the oxygen isotopic composition in
875  Leroy-Dos Santos, C., Masson-Delmotte, V., Casado, M., Fourré, E., Steen-Larsen, H. C., Maturilli, 
877  Record of Svalbard Water Vapor Isotopic Composition Documents Winter Air Mass Origin, Journal 
878  of Geophysical Research: Atmospheres, 125, e2020JD032681-e2020JD032681, 
880  Leroy-Dos Santos, C., Casado, M., Prié, F., Jossoud, O., Kerstel, E., Farradêche, M., Kassi, S., Fourré, 
881  E., and Landais, A.: A dedicated robust instrument for water vapor generation at low humidity for use 
882  with a laser water isotope analyzer in cold and dry polar regions, Atmospheric Measurement 
884  Li, C., Enrico, M., Magand, O., Araujo, B. F., Le Roux, G., Osterwalder, S., Dommergue, A., 
885  Bertrand, Y., Brioude, J., De Vleeschouwer, F., and others: A peat core Hg stable isotope 
886  reconstruction of Holocene atmospheric Hg deposition at Amsterdam Island (37.8 oS), Geochimica et 
888  Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N., Prestbo, 
889  E., and Seigneur, C.: A synthesis of progress and uncertainties in attributing the sources of mercury in 
891  Lyman, S. N.; Jaffe, D. A. Formation and fate of oxidized mercury in the upper troposphere and lower 
893  Magand, O. and Dommergue, A.: Continuous measurements of atmospheric mercury at Maido 
894  Observatory (L2), Global Mercury Observation System [data set], 2022. 
895  Munksgaard, N. C., Zwart, C., Kurita, N., Bass, A., Nott, J., and Bird, M. I.: Stable isotope anatomy of 
897  Murphy, D. M.; Hudson, P. K.; Thomson, D. S.; Sheridan, P. J.; Wilson, J. C. Observations of Mercury- 
899  Noone, D.: Pairing Measurements of the Water Vapor Isotope Ratio with Humidity to Deduce 
900  Atmospheric Moistening and Dehydration in the Tropical Midtroposphere, Journal of Climate, 25, 
902  Pisso, I., Sollum, E., Grythe, H., Kristiansen, N. I., Cassiani, M., Eckhardt, S., Arnold, D., Morton, D., 
903  Thompson, R. L., Groot Zwaaitink, C. D., Evangelou, N., Sodemann, H., Haimberger, L., Henne, S., 
905  Lagrangian particle dispersion model FLEXPART version 10.4, Geoscientific Model Development, 
907  Polian, G., Lambert, G., Ardouin, B., and Jegou, A.: Long-range transport of continental radon in 
909  Risi, C., Bony, S., Vimeux, F., and Jouzel, J.: Water-stable isotopes in the LMDZ4 general circulation 
910  model: Model evaluation for present-day and past climates and applications to climatic interpretations 
911  of tropical isotopic records, Journal of Geophysical Research Atmospheres, 115, 
913  Sciare, J., Mihalopoulos, N., and Dentener, F.: Interannual variability of atmospheric dimethylsulfide 
914  in the southern Indian Ocean, Journal of Geophysical Research: Atmospheres, 105, 26369–26377, 
915  2000.


Sprovieri, F., Perrone, N., Benedcardino, M., D’amore, F., Carbone, F., Cinnirella, S., Mannarino, V.,
Landis, M., Ebihngaus, R., Weigelt, A., and others: Atmospheric mercury concentrations observed at ground-based monitoring sites globally distributed in the framework of the GMOS network, Atmospheric chemistry and physics, 16, 11915–11935, 2016.

Jouzel, J., Popp, T., Sheldon, S., Simonsen, S. B., Sjolte, J., Steffensen, J. P., Sperlich, P.,


Stevens, B., Giorgetta, M., Esch, M., Mauritsen, T., Crueger, T., Rast, S., Salzmann, M., Schmidt, H.,
Bader, J., Block, K., Brokopf, R., Fast, I., Kinne, S., Kornblueh, L., Lohmann, U., Pulmanns, R.,

Swartendruber, P., Chand, D., Jaffe, D., Smith, J., Reimblender, D., Gratz, L., Keeler, J., Strode, S.,


Talbot, R., Mao, H., Scheuer, E., Dibb, J., Avery, M., Browell, E., Sachse, G., Vay, S., Blake, D., Huey, G., and others: Factors influencing the large-scale distribution of Hg in the Mexico City area and over the North Pacific, Atmospheric Chemistry and Physics, 8, 2103–2114, 2008.


