Stable water isotope fractionation processes
in weather systems and their influence on
isotopic variability on different time scales

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Abstract

Stable water isotopes are naturally available tracers of moist processes in the atmosphere. Due to their different mass and symmetry they experience fractionation during phase transitions and thereby record information about the condensation and evaporation history of air parcels. They can be used to study sources and transport of atmospheric moisture or as climate proxies to reconstruct past temperature changes from measurements in paleoarchives. The isotopic composition of atmospheric moisture varies largely on different time scales. However, the dynamical and physical processes influencing the isotopic variability are complex and not completely understood so far, in particular on short (hourly to daily) time scales. The application of numerical models is a useful way of studying these processes. They provide the full four-dimensional structure of the isotope fields and can be used for sensitivity tests to quantify the role of specific mechanisms for isotopic variability. In this thesis, atmospheric stable water isotope processes are investigated with the help of different numerical model simulations. The aim is to improve our understanding of the hourly to seasonal variations of $\delta^{2}H$ and deuterium excess in water vapour and precipitation, with a focus on Europe.

In the first part of the thesis, a simple Rayleigh model simulating the isotopic composition of air parcels during moist adiabatic ascent is used to study the impact of the nonequilibrium effect, the temperature effect, and the nonlinear effect of the $\delta$ scale on deuterium excess. The $\delta$ scale effect is important especially in depleted air parcels, for which it can change the sign of the deuterium excess in the remaining vapour from negative to positive. In this case the deuterium excess to a large extent reflects an artefact of its own definition, which overwrites both the nonequilibrium and the temperature effect. We propose an alternative definition of the deuterium excess that solves this problem, as it is based on the logarithmic scale and therefore not affected by the nonlinearity of the $\delta$ scale.

In the second part of the thesis, stable water isotopes are simulated in an idealised extratropical cyclone using the isotope-enabled version of the COSMO model (COSMOiso). A set of experiments with differing initial conditions of $\delta^{2}H$ in vapour and partly deactivated isotopic fractionation allows quantifying the relative roles of cloud fractionation and vertical and horizontal advection for the simulated $\delta^{2}H$ signals associated with the cyclone and its fronts. Horizontal transport determines the large-scale
pattern of $\delta^2$H in both vapour and precipitation, while fractionation and vertical transport are more important on a smaller scale, near the fronts. During the passage of the cold front fractionation leads to a V-shaped pattern of $\delta^2$H in precipitation and vapour, which is, for vapour, superimposed on a gradual decrease caused by the arrival of colder air masses.

Finally, in the third part of the thesis, realistic COSMOiso simulations are performed over Europe for the years 2002–2011, with input data from two different general circulation models (IsoGSM and ECHAMwiso). The nested COSMOiso simulations show an improved performance compared to the general circulation models, underlining the added value of simulating stable water isotopes with high resolution numerical models. Linear correlations of $\delta^2$H and deuterium excess with meteorological variables highlight the important role of temperature and relative humidity for the variability of $\delta^2$H and deuterium excess, respectively. Furthermore, a new Lagrangian method for quantifying the impact of different processes on isotopes along trajectories shows that evaporation from the ocean, evaporation from land, and mixing with moister air are the most important processes determining climatological mean $\delta^2$H and deuterium excess at low levels, while cloud formation processes are important for their variability.

In summary, this thesis applies different numerical model simulations to disentangle the complex interactions of meteorological processes involving isotopic fractionation, and provides new insight into how they shape the isotopic composition of water vapour and precipitation. This is a step towards a better understanding of the mechanisms responsible for isotopic variations in atmospheric moisture and towards the overall aim of using stable water isotopes as tracers of key processes in the atmospheric water cycle.
Zusammenfassung


Im zweiten Teil der Arbeit werden mit der Isotonversion des COSMO-Modells (COSMOiso) stabile Wasserisotope in einer idealisierten extratropischen Zykline simuliert. Eine Zusammenstellung von Experimenten mit verschiedenen Anfangsbedingungen
von $\delta^2$H in Wasserdampf und teilweise deaktivierter isotopischer Fraktionierung ermöglicht eine Quantifizierung der relativen Einflüsse von Vertikal- und Horizontaltransport sowie Fraktionierung innerhalb und unterhalb von Wolken auf das $\delta^2$H-Signal in der Zyklone und an ihren Fronten. Horizontaltransport bestimmt das grossskalige Muster von $\delta^2$H in Wasserdampf und Niederschlag, während Fraktionierung und Vertikaltransport auf kleineren Skalen wichtig sind, besonders in der Nähe der Fronten. Während dem Durchgang der Kaltfront führt Fraktionierung zu einem V-förmigen Verlauf von $\delta^2$H im Niederschlag und Dampf, der im Dampf von einer allmählichen Abnahme durch die Ankunft kälterer Luftmassen überlagert ist.


Chapter 1

Introduction

In 1910, Frederick Soddy explored the radioactive decay chain of thorium and discovered that its product mesothorium I was chemically inseparable from the element radium, although its atomic weight differed by about two units (Soddy, 1911). From this and other experiments he inferred that atoms with different weight can occupy the same place in the periodic table (Figure 1.1), disproving the second postulate of John Dalton’s Atomic Theory, that atoms of an element are identical in weight, shape, and size. Soddy called these atoms isotopes, which in Greek means ‘same place’ (Soddy, 1913). This conclusion was reached simultaneously by Kazimierz Fajans (Fajans, 1913a,b) and was later confirmed by Sir J. J. Thomson, who built a so-called positive ray apparatus and found evidence for two different kinds of neon atoms ($^{20}\text{Ne}$ and $^{22}\text{Ne}$) (Thomson, 1913). The apparatus was a predecessor of today’s mass spectrometers, in which particles were ionised and deflected by electric and magnetic fields, following individual paths (‘parabolas’) according to their charge-to-mass ratio. Francis W. Aston refined the apparatus around 1919, and subsequently detected 205 of 287 naturally occurring isotopes (Aston, 1925, 1927; Thoennessen, 2016). The reason for their existence, however, only became clear in 1932, when James Chadwick discovered the neutron (Chadwick, 1932). Since then it is known that isotopes are atoms with the same number of protons, but a different number of neutrons, and therefore a different atomic weight.

Meanwhile, attempts were made to understand thermodynamic differences between isotopes. Frederick A. Lindemann applied statistical methods to derive the differences in vapour pressures of two kinds of lead isotopes with atomic weight 207.19 and 206.34, respectively (Lindemann, 1919). He calculated that, if the at that time controversial zero-point energy (the energy of a system at $T = 0\, \text{K}$) existed, the lighter isotope would have a slightly higher vapour pressure than the heavy isotope, while a much larger effect of the opposite sign was expected if the zero-point energy did not exist. His experiments showed that the vapour pressures were identical (within the limits of error), and he concluded that a zero-point energy must exist. This conclusion
was correct, however it was unfortunate that he performed the experiment on a heavy element, since the difference in thermodynamic properties of isotopes diminishes with increasing atomic weight (Urey, 1947). Twelve years later, Willem H. Keesom and Herman van Dijk found that the light neon isotope $^{20}\text{Ne}$ was indeed more volatile than the heavy neon isotope $^{22}\text{Ne}$ (Keesom and Van Dijk, 1931), and Harold C. Urey, Ferdinand G. Brickwedde and George M. Murphy estimated a large difference between the vapour pressures of still unknown hydrogen isotopes, and consequently detected $^2\text{H}$ through fractional distillation of liquid hydrogen (Urey et al., 1932). According to its atomic weight of $\sim 2$, they named it deuterium, which in Greek means ‘second’.

Due to their slightly different thermodynamic properties, isotopes became very useful tracers in various scientific disciplines. In 1947, Urey calculated equilibrium constants for a large number of isotope exchange reactions (Urey, 1947). They were 0 (or $\infty$) at $T = 0\ \text{K}$ and increased (or decreased) with increasing temperature. Urey recognised that this temperature dependence could be used to determine past temperatures from isotope measurements in paleoarchives, e.g., carbonate rocks. Samuel Epstein, a postdoctoral researcher in Urey’s group, and colleagues tested this idea by growing marine shelled animals under controlled temperatures (Epstein et al., 1951, 1953).
They found an empirical relationship between temperature and the oxygen isotope ratio in the samples, which was in good agreement with the theoretical predictions. In the following years, isotope ratios were measured in foraminifera (e.g., Emiliani, 1955), ice cores (e.g., Dansgaard et al., 1969), trees (e.g., Epstein et al., 1976) and other paleoarchives to reconstruct temperatures of the past. This provided entirely new insight into the history of Earth’s climate.

In atmospheric and hydrological sciences, the water molecules containing different isotopes of hydrogen and oxygen ($\text{H}_2\text{O}^{16}$, $\text{HD}^{16}$O, $\text{H}_2\text{O}^{17}$ and $\text{H}_2\text{O}^{18}$) proved to be a helpful means for better understanding the hydrological cycle. Due to their different mass and symmetry, these water isotopologues (hereafter referred to as water isotopes) experience fractionation during phase transitions (hence, their relative concentrations change) and can therefore record information about evaporation and condensation processes during the transport of air parcels. In 1961, the International Atomic Energy Agency (IAEA) and the World Meteorological Organisation (WMO) initiated the Global Network of Isotopes in Precipitation (GNIP), a world-wide survey of stable (and initially also radioactive) water isotopes in monthly precipitation, with the aim to collect systematic data of the isotopic composition of precipitation and characterise its spatial and temporal variability (Rozanski et al., 1993). Willi Dansgaard analysed the GNIP measurements in 1964, and found that the isotope values correlate linearly with surface temperature, but also vary with latitude, altitude, season, distance from the coast, and precipitation amount (Dansgaard, 1964; Figure 1.2). These isotope effects have remained valid until today, and characterise the climatological mean isotopic composition of precipitation (Figure 1.3).

On short time scales, variations in atmospheric circulation and meteorological processes can lead to considerable deviations from the mean state. Isotope measurements in hurricanes and tropical cyclones (e.g., Ehhalt and Östlund, 1970; Nicolini et al., 1989; Lawrence and Gedzelman, 1996; Munksgaard et al., 2015) revealed that these storms produce anomalously depleted precipitation (i.e., with substantially less heavy water isotopes than normal). Extratropical cyclones also showed a distinct isotopic signal, often in the form of a descending or V-shaped trend (e.g., Rindsberger et al., 1990; Celle-Jeanton et al., 2004; Barras and Simmonds, 2009; Aemisegger et al., 2015; see Section 1.2.2). The distribution of isotopes in the storms was usually closely linked to their structure and evolution. Thanks to this, the isotopes could be used for studying the dynamics of weather systems. For example, they helped to determine moisture source locations (Lawrence et al., 1982), or derive information about cloud microphysics (Smith, 1992). However, the interactions of processes involving isotopic fractionation are complex and still not perfectly understood. Therefore the potential of water isotopes as meteorological recorders has not yet been fully explored.
This thesis will focus on isotopic fractionation processes associated with weather systems over Europe (in particular, extratropical cyclones and fronts) and their impact on variations of stable water isotopes in water vapour and precipitation. We use the newly developed isotope version of the Consortium for Small-Scale Modelling (COSMO) model (Steppeler et al., 2003; Pfahl et al., 2012), which includes the water cycles of $\text{H}_2\text{O}$, $\text{HD}_2\text{O}$ and $\text{H}_2\text{H}_2\text{O}$, to simulate stable water isotopes with high temporal and spatial resolutions. The aim is to improve our understanding of the mechanisms driving isotopic variability on hourly to yearly time scales. In the following, Section 1.1 explains the concepts and definitions of stable water isotope physics, Section 1.2 describes relevant isotope processes in the atmospheric water cycle and in extratropical cyclones, Section 1.3 gives an overview over different methods of stable water isotope modelling, and Section 1.4 presents the objectives and outline of the thesis.

![Figure 1.2](image-url)

**Figure 1.2:** The annual mean $\text{H}_2\text{H}_2\text{O}/\text{H}_2\text{O}$ ratio of precipitation (expressed as $\delta^{18}\text{O}$, see Section 1.1.1 for definitions) as a function of the annual mean air temperature at surface. The numbers in parenthesis indicate the total thickness (in cm) of the investigated snow layers (from Dansgaard, 1964).
1.1 Stable water isotope physics

1.1.1 Definitions

The abundance of stable water isotopes is quantified with the isotope ratio $R$, which is defined as the ratio of the concentrations between the heavy and light isotope:

$$ R^{18}_{O} = \frac{[H_2^{18}O]}{[H_2^{16}O]}, \quad R^{2}_{H} = \frac{[HD^{16}O]}{[H_2^{16}O]} \quad (1.1) $$

Since the heavy stable water isotopes are much less abundant than the light stable water isotope (see Table 1.1), isotope ratios are commonly expressed in $\delta$ notation, relative to a standard. The usual standard is the Vienna Standard Mean Ocean Water (V-SMOW) ratio, which was defined by the IAEA.

$$ \delta = \frac{R_{sample} - R_{std}}{R_{std}} = \frac{R_{sample}}{R_{std}} - 1 \quad (\text{in } ^{\circ}/_{oo}) \quad (1.2) $$
Variations of stable water isotope ratios are caused by their different thermodynamic properties leading to isotopic fractionation during phase transitions. Thereby it is important to distinguish between equilibrium fractionation and nonequilibrium fractionation.

### 1.1.2 Equilibrium fractionation

Equilibrium fractionation results from a reversible process that occurs during a (thermodynamic) equilibrium reaction \((A \rightleftharpoons B)\). An example is the coexistence of liquid water and vapour. Heavier isotopes generally have higher binding energies, thus, they preferentially go to the compound in which the molecules are bound most strongly, in this case liquid water. The isotope ratios of the two phases (liquid and vapour) in isotopic equilibrium can be compared by the equilibrium fractionation factor:

\[
\alpha^{l/v}_{eq} = \frac{R_l}{R_v}
\]  

\(\alpha^{l/v}_{eq} > 1\) means that the heavy isotopes are enriched in the liquid phase. Sometimes also the reciprocal value \(\alpha^{v/l}_{eq}\) is used \((\alpha^{v/l}_{eq} = 1/\alpha^{l/v}_{eq})\). Equilibrium fractionation is temperature dependent, thus, for the liquid to vapour transition, \(\alpha^{l/v}_{eq}\) is larger for low temperatures and fractionation is therefore most pronounced in a cold environment. Equilibrium fractionation occurs during every fractionating phase transition, and is roughly eight times stronger for HD\(^{16}\)O than for H\(_2\)^{18}O. Hence, a ratio of 1:8 between \(\delta^{18}\)O and \(\delta^2\)H can often be found under equilibrium conditions.
1.1.3 Nonequilibrium fractionation

Nonequilibrium (or kinetic) fractionation results from an irreversible process, when the reaction is forced towards one side of the reaction equation ($A \rightarrow B$). Here the diffusion velocities of the isotopes are important. Heavy isotopes have slower diffusion velocities than light isotopes, thus they need more time to reach an equilibrium state. This leads to additional fractionation.

In the atmosphere, nonequilibrium fractionation occurs mainly during two processes (see also Section 1.2.1): (1) evaporation of liquid water from the surface or from rain drops, when there is a strong gradient of relative humidity, and winds transport the evaporate away from the source, and (2) the formation of mixed phase and ice clouds, which usually occurs in an environment that is supersaturated with respect to ice (Rogers, 1979).

Since $H_{18}^{2}O$ is heavier than $HD^{16}O$, nonequilibrium fractionation is slightly stronger for $H_{18}^{2}O$ than for $HD^{16}O$ and therefore leads to deviations from the usual 1:8 ratio between $\delta^{18}O$ and $\delta^{2}H$. These second order effects can be quantified as the deuterium excess ($d$) (Dansgaard, 1964).

$$d = \delta^{2}H - 8 \cdot \delta^{18}O$$  \hspace{1cm} (1.4)

The average value of $d$ in meteoric waters is 10‰ (Craig, 1961), which indicates that atmosphere and ocean typically are out of thermodynamic equilibrium.

1.2 Stable water isotope processes in the atmosphere

1.2.1 Water cycle

The most relevant physical mechanisms of stable water isotope fractionation in the atmospheric water cycle are illustrated in Figure 1.4 and are briefly explained in this section (following Sodemann, 2006, and Dütsch, 2013).

1. Water evaporates from the ocean surface. Directly at the interface of water and air, the two phases are in isotopic equilibrium, with water vapour being depleted in heavy isotopes with respect to the sea surface. Above the sea surface, a laminar layer dominated by molecular diffusion forms the transition to the turbulent boundary layer. This is where nonequilibrium effects play an important role. The diffusion velocities of the isotopes are mainly influenced by the humidity gradient in the laminar layer.
2. Water is transported in the turbulent boundary layer. This happens without fractionation.

3. Water forms a liquid cloud. The heavy isotopes preferentially form the condensed phase, leaving the remaining water vapour depleted in heavy isotopes. This can realistically be described by a Rayleigh condensation process (see Section 1.3.1). For temperatures above the freezing point of water, the process is in isotopic equilibrium.

4. Water is transported over large scales. This happens without fractionation.

5. Water evaporates from the land surface. Evaporation from bare soil involves equilibrium and nonequilibrium fractionation, similar as from the ocean surface. Transpiration of plants is generally assumed to occur without fractionation, since the leaf water content is small compared to the transpiration flux. This assumption is valid on long time scales ($\geq$ days), whereas on short time scales variations in isotopic enrichment of leaf water have to be taken into account (Dongmann et al., 1974; Harwood et al., 1999).

6. Water falls as liquid precipitation. Thereby it equilibrates its isotopic composition with the surrounding moisture, the equilibration time depending on drop size and
relative humidity. Due to the decreasing vapour isotope ratios with altitude, the rain arriving at the surface is enriched in heavy isotopes compared to the rain at cloud base.

7. Water reevaporates from falling rain drops, meaning that the remaining rain becomes further enriched in heavy isotopes. Similar as for evaporation from the ocean surface, nonequilibrium effects are important for this process. Processes (6) and (7) can be summarised as below cloud processes.

8. Water forms an ice cloud. Since the vapour is usually supersaturated with respect to ice, this process is not in isotopic equilibrium. Therefore, an additional kinetic isotope effect has to be taken into account (Jouzel and Merlivat, 1984).

9. Water falls as solid precipitation. Unlike rain, snow does not equilibrate with its surrounding moisture as it falls through the air, due to the low diffusion coefficient of water molecules in ice. Hence, snow usually has a more depleted signal than rain when arriving at the surface.

1.2.2 Extratropical cyclones

Extratropical cyclones can strongly influence isotopic variability in water vapour and precipitation on synoptic time scales. Many studies have found that during cold (and warm) front passages, isotope ratios decrease notably and sometimes increase again (descending or V-shaped trend; see, e.g., Gedzelman and Lawrence, 1990; Rindsberger et al., 1990; Celle-Jeanton et al., 2004; Aemisegger et al., 2015). This happens due to the interaction of several processes, which are shown schematically in Figure 1.5, and described in the following.

1. The arrival of new air masses behind the front. Cold air masses are usually more depleted than warm air masses due to longer rainout history and stronger fractionation.

2. Formation of clouds at different heights. Clouds forming at higher levels, where moisture is more depleted, consequently lead to more depleted precipitation.

3. Progressive depletion during rainout. Warm air ascends over cold air and gets more and more depleted due to rainout.

4. Changes in below cloud interactions. High precipitation intensity involves high relative humidity and large rain drops. Hence there is less enrichment of rain through evaporation and equilibration. Additionally, a descending (ascending) melting layer leads to a shorter (longer) equilibration time and less (more) enrichment of rain.
Figure 1.5: Schematic cross section through an extratropical cyclone. The blue and red line indicate the cold and warm front, respectively, and the thick black arrow shows the wind direction. The numbers correspond to processes responsible for isotopic variations: (1) arrival of new air masses, (2) formation of clouds at different heights, (3) progressive depletion during rainout, (4) below cloud interactions.

1.3 Modelling of stable water isotopes

Numerical models have long been used to help in the interpretation of stable water isotope measurements. They provide information on isotopes at locations where no measurements can be performed, and can be used for sensitivity tests clarifying the specific role of underlying processes. This section provides an overview over the three main categories of stable water isotope models: Rayleigh models, general circulation models, and limited-area models. Rayleigh models are typically used in a Lagrangian framework, meaning that they follow individual air parcels and simulate their isotopic composition during transport. General circulation and limited-area models are Eulerian models, meaning that they consider grid points in a spatially and temporally discretised domain and simulate isotopes at fixed locations.

1.3.1 Rayleigh models

Rayleigh models describe isotopic fractionation between two reservoirs in an open system (i.e., where the products are removed directly after formation). They are mostly used for simulating the isotopic composition of isolated air parcels, in which water condenses and (immediately) falls out as precipitation. The condensing water is enriched in heavy isotopes by $\epsilon \approx \alpha^\nu - 1$ compared to its surrounding water vapour. The more water condenses, the more depleted becomes the remaining vapour, and, thus, also
the new condensate. The isotopic composition of the remaining water vapour can be described mathematically with the following equation:

\[
\frac{R}{R_0} = f^{\alpha_{lv}-1}
\]  

(1.5)

where \( R \) and \( R_0 \) are the isotope ratios at time \( t \) and \( t = 0 \), respectively, \( f \) is the fraction of remaining water vapour, and \( \alpha_{lv} \) is the fractionation factor (\( \alpha_{lv} > 1 \)). The equation was introduced by Lord Rayleigh for the distillation of binary mixtures (Rayleigh, 1902) and is known as the Rayleigh condensation (or distillation) equation (see Appendix A.1 for a detailed derivation). Under equilibrium conditions and with a constant fractionation factor of \( \alpha^{18}O_{lv} = 1.01 \) (neglecting the temperature dependence), the isotopic compositions of the water vapour (\( \delta^{18}O_v \)), instantaneous condensate (\( \delta^{18}O_{\text{inst.}} \)), and

![Figure 1.6: Isotopic composition of vapour (\( \delta^{18}O_v \), solid light blue line), instantaneous condensate (\( \delta^{18}O_{\text{inst.}} \), dashed dark blue line) and accumulated condensate (\( \delta^{18}O_{\text{acc.}} \), dotted dark blue line) during a Rayleigh condensation process with water condensing from vapour. The fractionation factor between the condensate and the vapour is constant (\( \alpha^{18}O_{lv} = 1.01 \), \( \epsilon \approx 10^{\circ} \)). For comparison, the straight light and dark grey lines show the isotopic composition of vapour and liquid that would result from condensation in a closed system, where the condensate is kept inside the air parcel.](image-url)
accumulated condensate ($\delta^{18}\text{O}_{c}^{\text{acc.}}$) follow the curves depicted in Figure 1.6. $\delta^{18}\text{O}_{v}$ and $\delta^{18}\text{O}_{c}^{\text{inst.}}$ decrease exponentially and in parallel with a distance of $\epsilon \approx 10\%_{oo}$. $\delta^{18}\text{O}_{c}^{\text{acc.}}$ decreases more slowly, and, after all vapour has condensed, is equal to $\delta^{18}\text{O}_{v}$ in the beginning.

The Rayleigh condensation equation (Equation 1.5) was used by Dansgaard (1964), among others, for simulating isotopic fractionation during rain formation in cooling air parcels. With his model, Dansgaard was able to explain the distribution of stable water isotopes in global precipitation and define the isotope effects. Since then, Rayleigh models have been refined by including fractionation during evaporation from the ocean and the presence of liquid in the air parcels (Merlivat and Jouzel, 1979), evapotranspiration (Rozanski et al., 1982), nonequilibrium effects during ice cloud formation (Jouzel and Merlivat, 1984), and the Wegener-Bergeron-Findeisen process in mixed phase clouds, where the water droplets tend to evaporate in favour of the ice crystals (Ciais and Jouzel, 1994). However, as they use idealised transport paths, these models still strongly simplify the complexity of the global water cycle (Hoffmann et al., 2000). Most recent Rayleigh models (e.g., Helsen et al., 2004; Pfahl and Wernli, 2009; Christner et al., 2017) simulate fractionation along realistic trajectories and hence are able to account for the variability of transport paths and the mixing of air masses with different origin. They provide a direct link to the most important processes and moisture sources, while still having a relatively simple numerical structure.

1.3.2 General circulation models

Atmospheric general circulation models (GCMs) simulate Earth’s atmosphere by solving the equations expressing conservation of momentum (Navier-Stokes equation), energy (thermodynamic equation), and mass (continuity equation) on a global grid. They assume hydrostatic equilibrium and have a typical horizontal resolution between $1^\circ$ and $10^\circ$.

Following the work of Joussaume et al. (1984), who implemented stable water isotopes in the GCM of the Laboratoire de Météorologie Dynamique (LMD), several other GCMs were equipped with isotopes: among others, the European Centre Hamburg Model (ECHAM; Hoffmann et al., 1998; Werner et al., 2011), the National Center for Atmospheric Research Community Atmospheric Model (NCAR CAM; Lee et al., 2007), the Goddard Institute for Space Studies Model (GISS; Jouzel et al., 1987; Schmidt et al., 2007), and the Global Spectral Model (GSM; Yoshimura et al., 2008). The implementation is always based on the same principle: parallel water cycles are introduced and all prognostic moisture variables (e.g., vapour, liquid clouds) are duplicated for each of the heavy isotopes (HD$^{16}$O, H$_2^{18}$O, and most recently H$_2^{17}$O). These additional variables experience the same physical processes as the light isotope, i.e., they are
advec ted by winds and form clouds and precipitation. Every time a phase transition occurs, equilibrium and nonequilibrium fractionation are computed for the involved water species, which modifies their isotopic composition. See, e.g., Sturm et al. (2010) for a detailed model description.

Isotope-enabled GCMs can be used for process studies of the large scale water cycle, and to support the interpretation of stable water isotope measurements in paleoclimate archives. At the same time they allow for a direct validation of paleoclimate simulations with measurements, while there are no observations available of temperature, precipitation, or atmospheric pressure prior to 1750 (Sturm et al., 2010).

1.3.3 Limited-area models

Regional climate models

Regional climate models (RCMs) work similarly as GCMs, but cover a limited domain and therefore typically have a higher resolution (down to 1 km), which allows them to reproduce processes over complex terrain and synoptic-scale features like cyclones and fronts more accurately than GCMs. Boundary conditions for RCMs are provided by GCMs.

Sturm et al. (2005) incorporated stable water isotopes in the Regional Model (REMO), which was subsequently used for climatological studies, e.g., over South America (Sturm et al., 2007) and Svalbard (Divine et al., 2011). Yoshimura et al. (2010) developed the isotope version of the Regional Spectral Model (RSM) and used it for a case study of an atmospheric river event at the US west coast. These two regional models show an improved representation of isotopic processes taking place in mountain areas compared to GCMs, but due to their still rather simple cloud microphysics and hydrostatic numerics, they are limited in capturing mesoscale atmospheric features.

Pfahl et al. (2012) incorporated isotopes in the COSMO model, which is a weather forecast and climate model that was developed for small-scale operational predictions (Steppeler et al., 2003; Baldauf et al., 2011) and is used at several European weather services. The COSMOiso model includes an advanced microphysical scheme and nonhydrostatic dynamics, which makes it very suitable for simulating stable water isotopes in weather systems.

A compromise between standard GCMs and RCMs are global models with the functionality of stretching the global grid or nesting a finer regional grid within the coarser global grid. Examples for isotope models are LMDZ-iso (with Z for Zoom) (Risi et al., 2010a) and the isotope version of the Icosahedral Nonhydrostatic Model with the extension for Aerosol and Reactive Trace gases (ICON-ART-Iso), which is currently under development (Eckstein et al., 2016).
Cloud resolving and large eddy simulation models

GCMs and RCMs rely on physical parameterisations, which statistically represent processes occurring on subgrid scales, e.g., convection, radiative transfer, or boundary layer turbulence. Consequently, simulated isotope ratios are sensitive to empirical parameters used for these parameterisations (Bony et al., 2008; Lee et al., 2009; Galewsky et al., 2016). Cloud resolving models (CRMs) have grids that are fine enough to resolve some of these processes, including deep convection. Large eddy simulation (LES) models also resolve shallow convection and part of the boundary layer turbulence.

Stable water isotopes have been implemented in two CRMs and one LES model so far: the Distributed Hydrodynamic Aerosol and Radiation Modeling Application (DHARMA; Smith et al., 2006), the System for Atmospheric Modeling (SAM; Blossey et al., 2010) and the NCAR-LES model (Lee et al., 2012). Furthermore, COSMOiso can also be used in cloud resolving mode. Apart from providing the opportunity to explicitly study convection and turbulence and their influence on isotopes, CRMs and LES models can also be compared to stand-alone versions of parameterisation schemes used in GCMs and RCMs and thereby help in their evaluation and development (Galewsky et al., 2016).

1.4 Objectives and outline

The aim of this thesis is to study and better understand short and long term variations of $\delta^2$H and deuterium excess in water vapour and precipitation over Europe. In particular, we focus on the following questions:

1. What determines $\delta^2$H and deuterium excess during the transport of air masses in an air parcel perspective?

2. How do extratropical cyclones influence transport and fractionation of stable water isotopes?

3. Which meteorological processes are responsible for isotopic variations on hourly to yearly time scales?

The questions are addressed with numerical model simulations of increasing complexity, from a highly idealised Rayleigh model simulating the isotopic composition of an isolated air parcel during moist adiabatic ascent to realistic 10-year simulations of stable water isotopes over Europe using COSMOiso. In Chapter 2, the Rayleigh model, COSMOiso and its land surface model TERRAiso are described in more detail. In Chapter 3, the Rayleigh model is applied to study the impact of three different effects...
(nonequilibrium effect, temperature effect, and the nonlinearity of the δ scale) on the deuterium excess, and an alternative exponential definition of the deuterium excess is tested. In Chapter 4, COSMOiso is used in an idealised baroclinic channel framework simulating an isolated extratropical cyclone to study its impact on advection and fractionation of isotopes. In Chapter 5, realistic 10-year simulations over Europe are presented, again with COSMOiso, and long-term impacts of meteorological processes on isotopes are analysed. Chapter 6 summarises the main findings of the thesis and provides an overview of potential future research questions.
Isotope models

2.1 Rayleigh model

The Rayleigh model used in this thesis is in line with those developed by Merlivat and Jouzel (1979) for the liquid phase and Jouzel and Merlivat (1984) for the solid phase, with the difference that the condensate is immediately removed from the air parcels also for the liquid phase and that mixed phase clouds exist in a certain temperature range (between $T = -23^\circ C$ and $T = 0^\circ C$). In contrast to the more complex model by Ciais and Jouzel (1994), our model assumes that liquid and solid parts of the cloud are spatially separated and do not interact with each other. Thus, it neglects the Wegener-Bergeron-Findeisen process, where for the coexistence of both phases the water droplets tend to evaporate in favour of the ice crystals.

2.1.1 Moist adiabatic ascent of the air parcels

The Rayleigh model simulates a moist adiabatic ascent of isolated air parcels. They start at the height level $z_0$ with pressure $p_0$, temperature $T_0$ and relative humidity $h_0 = 100\%$, and ascend in height steps of $\Delta z$. At every height level $z_k$ the moist adiabatic lapse rate $\Gamma_m$ is calculated following Holton (2004):

$$\Gamma_m = \frac{g}{c_p} \cdot \frac{1 + L_v w_k/(R_d T_k)}{1 + \epsilon L_v^2 w_k/(c_p R_d T_k^2)}$$

where $g$ is the gravitational acceleration, $c_p$ is the specific heat of dry air, $L_v$ is the latent heat of vaporisation of water, $R_d$ is the specific gas constant of dry air, $T_k$ is the temperature of the air parcel at level $z_k$, $\epsilon$ is the ratio of the specific gas constants of dry air and water vapour, and $w_k$ is the mixing ratio of the air parcel at level $z_k$. 
From the lapse rate at level $z_k$ and using the barometric equation, the temperature $T_{k+1}$ and pressure $p_{k+1}$ at the higher level $z_{k+1} = z_k + \Delta z$ can be derived:

$$
T_{k+1} = T_k - \Gamma_m \Delta z \tag{2.2}
$$

$$
p_{k+1} = p_k \cdot \left(\frac{T_{k+1}}{T_k}\right)^\frac{\gamma}{\gamma-1} \tag{2.3}
$$

We assume that all moisture above saturation condenses and immediately falls out from the air parcel as precipitation. Thus, the new mixing ratio $w_{k+1}$ and specific humidity $q_{k+1}$ can be diagnosed as:

$$
w_{k+1} = \epsilon \cdot \frac{e^*}{p_{k+1} - e^*} \tag{2.4}
$$

$$
q_{k+1} = \frac{w_{k+1}}{1 + w_{k+1}} \tag{2.5}
$$

where $e^*$ is the saturation vapour pressure in the air parcel, which is defined as a combination of the saturation vapour pressure over liquid water $e^*_l$ and over ice $e^*_i$:

$$
e^* = f^C_l \cdot e^*_l + f^C_i \cdot S_i \cdot e^*_i \tag{2.6}
$$

Here, $f^C_l$ and $f^C_i = 1 - f^C_l$ are the liquid water and ice fraction of the condensate, respectively. For $T > 0^\circ C$ the condensate is purely liquid ($f^C_l = 1$), for $T < -23^\circ C$ it is purely ice ($f^C_i = 0$). For $-23^\circ C < T < 0^\circ C$ the condensate is mixed phase and $f^C_l$ is interpolated quadratically between 0 and 1. $S_i$ is the supersaturation with respect to ice and is prescribed as $S_i = e^*_l / e^*_i$ for $T = 0^\circ C$ and as $S_i = 1 - \lambda T$ for $T < -23^\circ C$ with $\lambda = 0.004$ (as in Risi et al., 2010a). For $-23^\circ C < T < 0^\circ C$ $S_i$ is also interpolated quadratically.

Finally, the new fraction of remaining water vapour is given by:

$$
f_{k+1} = \frac{q_{k+1}}{q_0} \tag{2.7}
$$

### 2.1.2 Stable water isotopes

For every height step, the isotope ratios in the remaining water vapour are calculated with the Rayleigh condensation equation (cf. Equation 1.5):

$$
\frac{R_{k+1}}{R_k} = \left(\frac{f_{k+1}}{f_k}\right)^{\alpha_{\text{eff}}-1} \tag{2.8}
$$
where $R_{k+1}$ and $R_k$ are the isotope ratios and $f_{k+1}$ and $f_k$ are the fractions of remaining water vapour at height level $z_{k+1}$ and $z_k$, respectively, and $\alpha_{\text{eff}}$ is a combined (effective) fractionation factor, defined as a combination of the equilibrium fractionation factors with respect to liquid ($\alpha^{l/v}_{eq}$) and ice ($\alpha^{l/v}_{eq}$) and the nonequilibrium fractionation factor $\alpha_k$ (for $T < 0^\circ C$):

$$\alpha_{\text{eff}} = f_c^l \cdot \alpha^{l/v}_{eq} + f_c^i \cdot \alpha^{l/v}_{eq} \cdot \alpha_k$$  \hspace{1cm} (2.9)

with

$$\alpha_k = \frac{S_i \cdot D^{iso}}{\alpha^{l/v}_{eq} \cdot (S_i - 1) + D^{iso}}$$  \hspace{1cm} (2.10)

where $D^{iso}$ and $D$ are the diffusion coefficients of the heavy and light isotopes respectively. $\alpha^{l/v}_{eq}$ is parameterised following Majoube (1971a) and $\alpha^{l/v}_{eq}$ is parameterised following Merlivat and Nief (1967) for HD$^{16}$O and Majoube (1971b) for H$^{18}$O. The diffusion coefficients $D^{iso}$ and $D$ are taken from Merlivat (1978).

### 2.2 COSMOiso

COSMO (Steppeler et al., 2003) is a weather forecast and climate model that is operationally used at several European weather services. It is based on the hydrothermodynamical equations describing compressible nonhydrostatic flow and can be used for simulations with horizontal resolutions of less than 1km. The isotope implementation (Pfahl et al., 2012) is similar to other Eulerian isotope models (e.g., Joussaume et al., 1984; Sturm et al., 2005; Blossey et al., 2010; Werner et al., 2011): parallel water cycles are introduced for HD$^{16}$O and H$^{18}$O, which are used purely diagnostically and do not affect other model components. The heavy isotopes experience the same physical processes as the light isotope, except during phase transitions, when isotopic fractionation occurs. In the following, the parameterisations of isotopic fractionation used for these phase transitions are described (following Pfahl et al., 2012). For a detailed description of the standard physical parameterisations of COSMO see Doms et al. (2011).
2.2.1 Surface fluxes

Evaporation from the ocean

Fractionation during evaporation from the ocean is parameterised with the Craig-Gordon model, a linear resistance model that was introduced by Craig and Gordon (1965). It is based on the following equation:

\[ R'_{E_{oce}} = \alpha_k \cdot \frac{R'_{oce}/\alpha_{eq} - h \cdot R'_{atm}}{1 - h} \tag{2.11} \]

where \( R'_{E_{oce}} \) is the isotope ratio in the evaporation flux from the ocean, \( \alpha_k \) is the nonequilibrium fractionation factor, \( \alpha_{eq}/\nu \) is the equilibrium fractionation factor between liquid and vapour at the sea surface, \( R'_{oce} \) is the isotope ratio in the ocean, \( h \) is the relative humidity of the atmosphere, defined with respect to saturation at the sea surface temperature, and \( R'_{atm} \) is the isotope ratio in the atmosphere. \( R' \) is defined as:

\[ R' = \frac{R}{R_{VSMOW}} \tag{2.12} \]

The equilibrium fractionation factor \( \alpha_{eq}/\nu \) is parameterised following Majoube (1971a). For the nonequilibrium fractionation factor \( \alpha_k \) two options are implemented. The first one uses the classical formulation of \( \alpha_k \) as a function of wind speed by Merlivat and Jouzel (1979), the second one uses the constant (wind speed independent) value of \( \alpha_k \) from Pfahl and Wernli (2009).

Evaporation from land

Three options are implemented for evaporation from land. The first option uses external soil isotope concentrations from a GCM and assumes that no fractionation occurs during evaporation from land (i.e., the isotopic composition of the evaporation flux is equal to the isotopic composition of the soil). This assumption is used in most atmospheric isotope models (e.g., Yoshimura et al., 2008; Risi et al., 2010a; Werner et al., 2011). The second option also uses external soil isotope concentrations, but assumes that fractionation during bare soil evaporation occurs according to the Craig-Gordon model (Equation 2.11 with \( R'_{soil} \) instead of \( R'_{oce} \)). The third option uses the isotope version of the land surface model TERRA for calculating the water budget of the heavy isotopes in the soil. This model (TERRAiso) will be described in Section 2.3.
2.2 COSMO

2.2.2 Cloud microphysics

Fractionation is assumed to occur only during microphysical processes involving the vapour phase, including condensation of vapour to liquid cloud droplets and rain, evaporation of liquid cloud droplets and rain, and deposition of vapour on ice and snow. The other processes (freezing, melting and sublimation) occur without fractionation. In this nonfractionating case, the isotope transfer rate $S_{m,n}^{iso}$ of a heavy isotope from one phase $m$ to another phase $n$ can be expressed as:

$$S_{m,n}^{iso} = R'_m \cdot S_{m,n}$$  (2.13)

where $R'_m$ is the isotope ratio in phase $m$ and $S_{m,n}$ is the transfer rate of the light isotope. For the fractionating phase transitions the isotope ratio $R'_{S_{m,n}}$ in the flux $S_{m,n}$ from phase $m$ to phase $n$ can be smaller or larger than the isotope ratio $R'_m$ in phase $m$. The parameterisations used for these phase transitions are described in the following.

Liquid clouds

In COSMO the condensation and evaporation of liquid clouds is parameterised with a saturation adjustment technique, which implies that liquid cloud droplets are always in thermodynamic equilibrium with their surrounding vapour. This is also true for the heavy isotopes, since the equilibration time of cloud droplets is typically shorter than the time step applied in the model (In the order of a few seconds; Jouzel et al., 1975; Blossey et al., 2010). We denote the specific cloud water and water vapour content of the heavy isotopes before and after saturation adjustment as $q_{c}^{iso}$ and $q_{v}^{iso}$, and $q_{c,new}^{iso}$ and $q_{v,new}^{iso}$ respectively, and the specific cloud water and water vapour content of the light isotope after saturation adjustment as $q_{c,new}$ and $q_{v,new}$, respectively ($q_{c,new}$ and $q_{v,new}$ are equivalent to the total specific cloud and water vapour contents). The two conditions that the total water content of the isotopes is conserved:

$$q_{c,new}^{iso} + q_{v,new}^{iso} = q_{c}^{iso} + q_{v}^{iso}$$  (2.14)

and that the isotope ratios in the cloud droplets and in vapour are related by the equilibrium fractionation factor $\alpha_{eq}^{l/v}$:

$$\frac{q_{c,new}^{iso}}{q_{c,new}} = \alpha_{eq}^{l/v} \cdot \frac{q_{v,new}^{iso}}{q_{v,new}}$$  (2.15)
lead to the following equation for the change of the specific cloud water content of the heavy isotopes $\Delta q_{c}^{iso}$ (cf. Equation B21 in Blossey et al., 2010):

$$
\Delta q_{c}^{iso} = \frac{q_{v}^{iso} + q_{c}^{iso}}{1 + \frac{1}{\alpha_{eq}^{c/v}} \cdot \frac{q_{c,new}^{iso}}{q_{c,new}}} - q_{c}^{iso}
$$

(2.16)

$q_{c,new}^{iso}$ and $q_{v,new}^{iso}$ are then given by:

$$
q_{c,new}^{iso} = q_{c}^{iso} + \Delta q_{c}^{iso}
$$

(2.17)

$$
q_{v,new}^{iso} = q_{v}^{iso} - \Delta q_{c}^{iso}
$$

(2.18)

### Rain

For rain drops the assumption of isotopic equilibrium is not valid due to their larger size. Therefore the mass transfer of heavy isotopes between the rain drops and their surrounding vapour has to be modelled explicitly. In COSMOiso this is done by following the semi-empirical approach of Stewart (1975), in which the transfer rate of the heavy isotopes $S_{ev}^{iso}$ between rain drops and their surrounding water vapour is related to the transfer rate of the light isotope $S_{ev}$ by:

$$
S_{ev}^{iso} = S_{ev} \cdot \left( \frac{D_{iso}}{D} \right)^{n} \cdot q_{i}^{*} \cdot \frac{1}{\alpha_{eq}^{c/v}} \cdot \frac{q_{r}^{iso} - q_{v}^{iso}}{q_{r}^{iso} - q_{v}}
$$

(2.19)

$D_{iso}$ and $D$ are the diffusion coefficients of the heavy and light isotopes respectively, $q_{i}^{*}$ is the saturation specific humidity with respect to liquid water, and $q_{r}^{iso}$ and $q_{r}$ are the specific rain water contents of the heavy and light isotopes, respectively. The exponent $n$ is set to 0.58 independent of the drop size (according to the empirically determined value from Stewart, 1975). In COSMO $S_{ev}$ is parameterised as:

$$
S_{ev} = F(q_{r}) \cdot (q_{i}^{*} - q_{v})
$$

(2.20)

where $F(q_{r})$ is a function depending on $q_{r}$. $S_{ev}$ is always $\geq 0$ (only evaporation, no condensation on rain drops). Combining Equation 2.19 and Equation 2.20 then gives the transfer rate of rain evaporation for the heavy isotopes:

$$
S_{ev}^{iso} = F(q_{r}) \cdot \left( \frac{D_{iso}}{D} \right)^{n} \cdot \left( q_{i}^{*} \cdot \frac{1}{\alpha_{eq}^{c/v}} \cdot \frac{q_{r}^{iso} - q_{v}^{iso}}{q_{r}^{iso} - q_{v}} \right)
$$

(2.21)
The rightmost term is the humidity gradient of the heavy isotopes from the drop surface to the surrounding vapour (0 if air is saturated and drop and vapour are in isotopic equilibrium). Hence, even if no net evaporation occurs ($S_{ev} = 0$), there can be a mass transfer of heavy isotopes between the rain drops and the surrounding vapour, if they are not in isotopic equilibrium. The diffusion coefficients $D^{iso}$ and $D$ are again taken from Merlivat (1978).

**Ice clouds and snow**

Isotopic fractionation during vapour deposition on ice and snow is parameterised following Jouzel and Merlivat (1984) and Blossey et al. (2010). Due to the low diffusivities of water molecules in ice, there is no homogenisation of isotopes in ice crystals and snow flakes. The water vapour only interacts with the isotopic composition of the outermost layer, which is assumed to be equal to the isotopic composition in the deposition flux. Nonequilibrium effects occurring due to supersaturation with respect to ice are parameterised using a combined (effective) fractionation factor $\alpha_{eff}$ as in Jouzel and Merlivat (1984) and Blossey et al. (2010):

$$\alpha_{eff} = \frac{S_i \cdot (1 + b_s) \cdot D^{iso,f^{iso}}_{D:T}}{S_i - 1 + \frac{1}{\alpha_{eq}^{i/v}} \cdot (S_i \cdot b_s + 1) \cdot \frac{D^{iso,f^{iso}}_{D:T}}{D_{T}}},$$

(2.22)

where $S_i$ denotes the supersaturation with respect to ice, $\alpha_{eq}^{i/v}$ is the equilibrium fractionation factor with respect to ice, $b_s$ is a correction factor for the supersaturation, and $f$ and $f^{iso}$ are the ventilation factors of the light and heavy isotopes, respectively. Note that Equation 2.22 is equivalent to Equation 2.10 multiplied by $\alpha_{eq}^{i/v}$ if $b_s = 0$ and $f^{iso}/f = 1$. The equilibrium fractionation factor with respect to ice $\alpha_{eq}^{i/v}$ is parameterised following Merlivat and Nief (1967) for HD$^{16}$O and Majoube (1971b) for H$_2^{18}$O. The ratio of the ventilation factors $f^{iso}/f$ is set to 1 for deposition on ice and to 0.995 for deposition on snow flakes (following Jouzel and Merlivat, 1984). The isotopic composition of the deposition flux $S_{v,i}$ is then given by:

$$R'_{S_{v,i}} = \alpha_{eff} \cdot R'_{v},$$

(2.23)

where $R'_{v}$ is the isotope ratio in vapour. In COSMO supersaturation is predicted prognostically and therefore does not need to be prescribed as a function of temperature (in contrast to, e.g., Jouzel and Merlivat, 1984; Risi et al., 2010a; Werner et al., 2011). For the purpose of comparison, the option for using a prescribed supersaturation is
implemented as well. In this case, supersaturation is calculated from temperature ($T$) as follows:

\[ S_i = 1 - \lambda \cdot (T - T_{\text{melt}}) \]  

(2.24)

where $T_{\text{melt}}$ is the melting temperature of water ($T_{\text{melt}} = 0^\circ\text{C}$) and $\lambda$ is a tuning parameter, which is set to 0.004 (Risi et al., 2010a).

### 2.2.3 Moist convection

COSMO uses a modified version of the Tiedtke mass flux scheme (Tiedtke, 1989) for the parameterisation of convection. The cloud model in this scheme uses saturation adjustment for both liquid water and ice. Therefore, for the calculation of the fractionation factor during ice formation (Equation 2.22), the supersaturation with respect to ice is prescribed as a function of temperature as in Equation 2.24. Liquid water is assumed to be in isotopic equilibrium with the surrounding water vapour and fractionation is parameterised similarly as described in Section 2.2.2 for liquid clouds. In a temperature range between $-23^\circ\text{C}$ and $0^\circ\text{C}$ clouds are assumed to consist of mixed phases and the isotopic composition of the condensate is interpolated quadratically between liquid and ice.

The Tiedtke scheme assumes that the convective downdrafts are saturated due to evaporation of falling rain. The isotopic composition of rain and vapour in the downdrafts is calculated like in the case of liquid clouds in Section 2.2.2. Below cloud base, the evaporation rate of rain is parameterised following Kessler (1969). This rate is scaled according to Equation 2.19 for the heavy isotopes. Furthermore, a tuning parameter $f_{\text{equ}}$ is implemented to adjust the equilibration fraction of rain below cloud base ($f_{\text{equ}} = 0$ means no additional equilibration, $f_{\text{equ}} = 1$ means total equilibration). Currently, $f_{\text{equ}}$ is set to 0.5.

### 2.3 TERRAiso

The soil model TERRA (Doms et al., 2011) provides the surface temperature and specific humidity for the COSMO model over land by calculating the energy and water budget in the soil. The isotope version TERRAiso (Aemisegger, 2015) additionally calculates the water budget of the heavy isotopes HD$^{18}O$ and H$_2^{18}O$. The relevant fluxes for the water budget and the isotope implementation are shown schematically in Figure 2.1. TERRA predicts the water contents of three reservoirs: the interception reservoir containing all surface liquid water including dew on plants and on the soil,
the snow reservoir containing snow, frozen water and rime, and the soil reservoir containing all water below the Earth’s surface.

In the **interception reservoir** the water content \( W_{\text{int}} \) depends on the rates of rain \( P_r \), evaporation or dew formation \( E_{\text{int}} \), percolation \( I_{\text{perc}} \) and the runoff from the interception reservoir \( N_{\text{int}} \):

\[
\rho_w \cdot \frac{\partial W_{\text{int}}}{\partial t} = \beta \cdot P_r + E_{\text{int}} - I_{\text{perc}} - N_{\text{int}} \tag{2.25}
\]

where \( \rho_w \) is the density of liquid water and \( \beta \) is the fraction of precipitation kept in the interception reservoir. In the **snow reservoir** the water content \( W_{\text{snow}} \) depends on the rates of snow \( P_{\text{snow}} \), sublimation or rime formation \( E_{\text{snow}} \), melting \( I_{\text{melt}} \) and runoff from the snow reservoir \( N_{\text{snow}} \):

\[
\rho_w \cdot \frac{\partial W_{\text{snow}}}{\partial t} = P_{\text{snow}} + E_{\text{snow}} - I_{\text{melt}} - N_{\text{snow}} \tag{2.26}
\]

The soil reservoir is divided into 8 soil layers. In the **first soil layer** \( k = 1 \) the water content \( W_1 \) depends on the rates of bare soil evaporation \( E_{bs} \), rain \( P_r \), percolation from the interception reservoir \( I_{\text{perc}} \), snow melt \( I_{\text{melt}} \), surface runoff due to limited infiltration \( N_{\text{infil}} \), transpiration of plants \( T_1 \), subsurface runoff in the first soil layer \( N_{g,1} \), melting of soil ice \( M_1 \), and the vertical transport of water \( F_{1,2} \) to or from the lower soil layer \( k = 2 \):

\[
\rho_w \cdot \frac{\partial W_1}{\partial t} = E_{bs} + (1 - \beta) \cdot P_r + I_{\text{perc}} + I_{\text{melt}} - N_{\text{infil}} + T_1 - N_{g,1} + M_1 + F_{1,2} \tag{2.27}
\]

In the **subsequent soil layers** \( k = 2 - 6 \) the water content \( W_k \) depends on the rates of plant transpiration \( T_k \), subsurface runoff from the soil layer \( N_{g,k} \), melting of soil ice \( M_k \), and the vertical transport of water \( F_{k-1,k} \) and \( F_{k,k+1} \) to or from the upper and lower soil layers:

\[
\rho_w \cdot \frac{\partial W_k}{\partial t} = T_k - N_{g,k} + M_k - F_{k-1,k} + F_{k,k+1} \tag{2.28}
\]

In every soil layer the soil ice content depends only on the melting of soil ice or freezing of liquid water \( M_k \):

\[
\rho_w \cdot \frac{\partial W_{\text{ice},k}}{\partial t} = -M_k \tag{2.29}
\]

Soil layer 7 is hydrologically inactive and uses a prescribed climatological soil water content. Soil layer 8 is also thermally inactive and uses a constant temperature set
Figure 2.1: Schematic of the water fluxes in TERRAiso (adapted from Aemisegger, 2015). Liquid and solid precipitation (\(P_r\) and \(P_{snow}\)) are given by the atmospheric part of COSMOiso, evapotranspiration (\(ET\)) is computed by TERRAiso. See text for details.

To the annual mean near surface air temperature. Note that the fluxes are defined positive toward the Earth’s surface (downward in the atmosphere, upward in the soil). Hence, \(P\), \(E\), \(I\) and \(T\) are positive downward and negative upward, while \(F\) is positive upward (capillary rise) and negative downward (gravitational flow). \(N\) is always positive, and \(M\) is defined positive from ice to liquid.

Precipitation (\(P_r\) and \(P_{snow}\)) is given by the atmospheric part of COSMO, the other fluxes are calculated by TERRA. The water budget is solved by first computing the evapotranspiration and infiltration fluxes and surface runoff due to infiltration excess, and then solving the Richards equation (Richards, 1931) for the vertical transport of
2.3 TERRAiso

water by capillary and gravitational forces. Finally, the water exceeding the field capacity of the soil is converted into subsurface runoff (separately for each soil layer). In TERRAiso the corresponding water budget of the heavy isotopes HD\textsuperscript{16}O and H\textsuperscript{18}O is computed diagnostically from the water budget of the light isotope H\textsuperscript{16}O. With $R' \equiv R/R_{\text{VSMOW}}$ this can be expressed as:

$$\rho_w \frac{\partial W_{\text{iso}}}{\partial t} = \rho_w \frac{\partial (R' \cdot W)}{\partial t} = \sum (R'_{S_i} \cdot S_i)$$ (2.30)

where $\sum (R'_{S_i} \cdot S_i)$ denotes the sum of the isotope fluxes in the water budget of a reservoir, and $R'_{S_i}$ corresponds to the isotope ratio in flux $S_i$. Hence, the water contents of the heavy isotopes in the interception reservoir ($R'_{\text{int}} \cdot W_{\text{int}}$), snow reservoir ($R'_{\text{snow}} \cdot W_{\text{snow}}$) and soil reservoir ($R'_{k} \cdot W_{k}$) are given by:

$$\rho_w \frac{\partial (R'_{\text{int}} \cdot W_{\text{int}})}{\partial t} = \beta \cdot R'_{P_r} \cdot P_r + R'_{E_{\text{int}}} \cdot E_{\text{int}}$$

$$- R'_{I_{\text{perc}}} \cdot I_{\text{perc}} - R'_{N_{\text{int}}} \cdot N_{\text{int}}$$ (2.31)

$$\rho_w \frac{\partial (R'_{\text{snow}} \cdot W_{\text{snow}})}{\partial t} = R'_{P_{\text{snow}}} \cdot P_{\text{snow}} + R'_{E_{\text{snow}}} \cdot E_{\text{snow}}$$

$$- R'_{I_{\text{melt}}} \cdot I_{\text{melt}} - R'_{N_{\text{snow}}} \cdot N_{\text{snow}}$$ (2.32)

$$\rho_w \frac{\partial (R'_{k} \cdot W_{k})}{\partial t} = \delta_{1,k} \cdot \left( R'_{E_{bs}} \cdot E_{bs} + (1 - \beta) \cdot R'_{P_r} \cdot P_r \right.$$}

$$+ R'_{I_{\text{perc}}} \cdot I_{\text{perc}} + R'_{I_{\text{melt}}} \cdot I_{\text{melt}} - R'_{N_{\text{infil}}} \cdot N_{\text{infil}} \right)$$

$$+ R'_{T_k} \cdot T_k - R'_{N_{g,k}} \cdot N_{g,k} + R'_{S_k} \cdot S_k$$

$$+ R'_{F_{k,k+1}} \cdot F_{k,k+1} - \left( 1 - \delta_{1,k} \right) \cdot R'_{F_{k-1,k}} \cdot F_{k-1,k}$$ (2.33)

where $\delta_{1,k}$ is the Kronecker delta being 1 for $k = 1$ and 0 for $k \neq 1$. The isotope ratios of precipitation ($R'_{P_r}$ and $R'_{P_{\text{snow}}}$) are given by the atmospheric part of COSMOiso, and the remaining isotope ratios are calculated by TERRAiso. The fluxes can be divided into three groups:

1. Nonfractionating fluxes

- Infiltration ($I_{\text{perc}}$ and $I_{\text{melt}}$)
- Vertical transport ($F_{k,k+1}$)
- Runoff ($N_{\text{infil}}, N_{\text{snow}}$ and $N_{g,k}$)
- Melting of soil ice ($M_k$)
• Snow sublimation \( (E_{\text{snow}} < 0) \)

2. Fractionating fluxes

• Bare soil evaporation \( (E_{bs}) \)
• Evaporation from the interception reservoir and dew formation \( (E_{\text{int}}) \)
• Rime formation \( (E_{\text{snow}} > 0) \)

3. Intermediate

• Plant transpiration \( (T_k) \)

Plant transpiration is often assumed to occur without fractionation (e.g., Washburn and Smith, 1934; Barnes and Allison, 1983), since in steady state the isotopic composition of water leaving the plants through transpiration is equal to the isotopic composition of water entering the plants from the soil. The steady state assumption is valid on long time scales \((\geq \text{days})\), however, on subdaily time scales variations in leaf water enrichment can occur and the isotopic composition of the transpiration flux is often different from the isotopic composition of the soil (Dongmann et al., 1974; Harwood et al., 1999; Wang et al., 2012). In TERRAiso both the nonfractionating (steady state) and fractionating (nonsteady state) version of plant transpiration are implemented.

### 2.3.1 Nonfractionating fluxes

For the nonfractionating fluxes the isotopes are passive tracers and the isotope ratio in the flux is equal to the isotope ratio in the reservoir, where the flux comes from. Hence:

• Infiltration:
  \[
  R'_{\text{perc}} = R'_{\text{int}} \\
  R'_{\text{melt}} = R'_{\text{snow}}
  \]

• Vertical transport:
  \[
  R'_{F,k+1} = R'_k \\
  = R'_{k+1} \quad \text{if } F_{k,k+1} < 0 \\
  \]

• Runoff:
  \[
  R'_{N_{\text{int}}} = R'_{\text{int}} \\
  R'_{N_{\text{snow}}} = R'_{\text{snow}} \\
  R'_{N_{\text{infil}}} = \frac{(1-\beta) \cdot R'_{P} \cdot P_r + R'_{\text{perc}} \cdot I_{\text{perc}}}{(1-\beta) \cdot P_r + I_{\text{perc}}}
  \]

• Melting of soil ice:
  \[
  R'_{M_k} = R'_{\text{ice},k} \quad \text{if } M_k > 0 \\
  = R'_k \quad \text{if } M_k < 0
  \]
• Snow sublimation: \( R'_{E_{\text{snow}}} = R'_{\text{snow}} \) if \( E_{\text{snow}} < 0 \)

### 2.3.2 Fractionating fluxes

The group of the fractionating fluxes can further be separated into equilibrium and nonequilibrium fluxes. The equilibrium fluxes are dew formation (\( E_{\text{int}} > 0 \)) and rime formation (\( E_{\text{snow}} > 0 \)). For these two fluxes the isotope ratios are calculated with the equilibrium fractionation factors over liquid (\( \alpha_{eq}^{l/v} \)) and ice (\( \alpha_{eq}^{i/v} \)):

- Dew formation: \( R'_{E_{\text{int}}} = \alpha_{eq}^{l/v} \cdot R'_{\text{atm}} \) if \( E_{\text{int}} > 0 \)
- Rime formation: \( R'_{E_{\text{snow}}} = \alpha_{eq}^{i/v} \cdot R'_{\text{atm}} \) if \( E_{\text{snow}} > 0 \)

where \( R_{\text{atm}} \) refers to the isotope ratio in the atmosphere at the lowest model level. The equilibrium fractionation factors are parameterised following Majoube (1971a) for \( \alpha_{eq}^{l/v} \) and following Merlivat and Nief (1967) and Majoube (1971b) for \( \alpha_{eq}^{i/v} \).

The nonequilibrium fluxes are bare soil evaporation (\( E_{bs} \)) and evaporation from the interception reservoir (\( E_{\text{int}} < 0 \)). For these two fluxes the isotope ratios are calculated with the Craig-Gordon model (Craig and Gordon, 1965):

- Bare soil evaporation: \( R'_{E_{bs}} = \alpha_k \cdot \frac{R'_{1}/\alpha_{eq}^{l/v} - h \cdot R'_{\text{atm}}}{1-h} \)
- Evaporation from the interception reservoir: \( R'_{E_{\text{int}}} = \alpha_k \cdot \frac{R'_{\text{int}}/\alpha_{eq}^{i/v} - h \cdot R'_{\text{atm}}}{1-h} \) if \( E_{\text{int}} < 0 \)

where \( R'_{1} \) and \( R'_{\text{int}} \) refer to the isotope ratios in the first soil layer and in the interception reservoir, respectively, \( h \) is the relative humidity with respect to the surface temperature, and \( \alpha_k \) is the nonequilibrium fractionation factor defined as the \( n \)th power of the molecular diffusivity ratio in air (Mathieu and Bariac, 1996):

\[
\alpha_k = \left( \frac{D_{iso}}{D} \right)^n \tag{2.34}
\]

with \( n = 0.67 \) (Riley et al., 2002). Thus, with the diffusion coefficients from Merlivat (1978), \( \alpha^{18O_k} = 0.981 \) and \( \alpha^{2H_k} = 0.984 \). The equilibrium fractionation factor \( \alpha_{eq}^{l/v} \) is again parameterised following Majoube (1971a).
2.3.3 Plant transpiration

Plant transpiration in TERRAiso can occur with or without fractionation. In the nonfractionating case (steady state), the isotope ratio in the plant transpiration flux is equal to the isotope ratio in the soil layer, where the water is taken up:

- Plant transpiration (nonfractionating): \( R'_{T_k} = R'_{k} \)

In the fractionating case (nonsteady state), the isotope ratio in the transpiration flux is calculated based on the model by Farquhar and Cernusak (2005) with a constant leaf water content (\( W_L \)):

- Plant transpiration (fractionating): \( R'_{T_k} = R'_{k} - \frac{W_L}{T_k} \cdot \frac{R'_{L,new} - R'_{L}}{\Delta t} \)

where \( R_L \) and \( R'_{L,new} \) are the isotope ratios in leaf water before and after transpiration and \( \Delta t \) is the time step. \( R'_{L,new} \) is calculated from \( R_L' \) and the isotope ratio in leaf water in steady state \( R'_L \) :

\[
R'_{L,new} = R'_L \cdot e^{-\frac{\Delta t}{\tau \alpha}} + R'_L s \cdot \left( 1 - e^{-\frac{\Delta t}{\tau \sigma}} \right)
\]  

(2.35)

where \( \tau \) and \( \sigma \) are given by:

\[
\tau = \frac{W_L}{T_k}
\]

(2.36)

\[
\sigma = \frac{\alpha_{eq}^{lv} \cdot (1 - h)}{\alpha_k}
\]

(2.37)

Here, \( h \) is the relative humidity of the air with respect to the temperature at the leaf surface. The steady state leaf water isotope ratio \( R'_{L,s} \) is calculated following Cuntz et al. (2007):

\[
R'_{L,s} = R'_{Es} \cdot \frac{1 - e^P}{P} + R'_k \cdot \left( 1 - \frac{1 - e^P}{P} \right)
\]

(2.38)

where \( R'_{Es} \) is the steady state isotope ratio in the leaf at the evaporation site, \( R'_k \) is the isotope ratio in soil layer \( k \), and \( P \) is the Péclet number describing the ratio between advection from the xylem to the evaporation site and diffusion from the evaporation site to the xylem.
The isotope ratio at the evaporation site \((R'_\text{Es})\) and the isotope ratio in the transpiration flux \((R'_\text{Tk})\) can be related with the Craig-Gordon model (similarly as for \(R'_{\text{oce}}\) and \(R'_{\text{Eoce}}\) in Equation 2.11). Since the steady state isotope ratio in the transpiration flux is equal to the isotope ratio in the soil (see above), \(R'_\text{Es}\) can be calculated as follows:

\[
R'_\text{Es} = \alpha_{\text{eq}}^{l/v} \cdot \left( \frac{R'_k \cdot (1 - h)}{\alpha_k} + h \cdot R'_{\text{atm}} \right)
\]  

(2.39)

Note that if the transpiration flux is large compared to the leaf water content \((T_k \gg W_L)\), the term \(\frac{W_L}{T_k} \cdot \frac{R'_{L,\text{new}} - R'_L}{\Delta t}\) in the equation for \(R'_T\) vanishes and the steady state assumption is valid \((R'_T = R'_k)\).
Chapter 3

The impact of the nonlinearity of the $\delta$ scale on the deuterium excess

3.1 Introduction

In global precipitation, $\delta^{2}H$ and $\delta^{18}O$ covary linearly with a slope of $\sim 8$, fitting the so-called global meteoric water line (GMWL) (Craig, 1961), where the slope results from the roughly 8 times stronger fractionation of HD$^{16}O$ compared to H$_2^{18}O$ under equilibrium conditions. The deuterium excess (Dansgaard, 1964) is used as a measure for nonequilibrium effects, as it reflects deviations from the 1:8 ratio of equilibrium fractionation between H$_2^{18}O$ and HD$^{16}O$. Nonequilibrium effects appear when phase transitions are irreversible (i.e., forced towards one side). In these cases the smaller diffusion velocities of HD$^{16}O$ and H$_2^{18}O$ compared to H$_2^{16}O$ lead to additional fractionation. This happens mainly during two processes: (1) evaporation of liquid water from the surface or from rain drops, when there is a strong gradient of relative humidity, and winds transport the evaporate away from the source, and (2) the formation of mixed phase and ice clouds, which usually occurs in an environment that is supersaturated with respect to ice (Rogers, 1979). Since H$_2^{18}O$ is heavier than HD$^{16}O$, nonequilibrium fractionation is slightly stronger for H$_2^{18}O$ than for HD$^{16}O$.

Due to its sensitivity to processes involving nonequilibrium effects, the deuterium excess provides information complementary to $\delta^{2}H$ and $\delta^{18}O$, which are mainly governed by equilibrium fractionation. For example, it can help detecting changes in moisture source conditions and locations associated with reorganisations of the atmospheric circulation (e.g., Jouzel and Merlivat, 1982; Masson-Delmotte et al., 2005; Sodemann et al., 2008a; Pfahl and Sodemann, 2014), tuning the supersaturation function for ice cloud parameterisations in atmospheric models (e.g., Petit et al., 1991; Werner et al., 2011), or diagnosing the fraction of moisture recycling and plant transpiration over land (e.g., Salati et al., 1979; Aemisegger et al., 2014).
However, the nonequilibrium effect is not the only factor influencing the deuterium excess. Another effect is the difference in the temperature dependence of the equilibrium fractionation factors. Equilibrium fractionation is more than 8 times stronger for HD\(^{16}\)O than for H\(^{18}\)\(_2\)O at temperatures below 22.5°C (\(\sim 8.7\) at \(T = 0^\circ\)C), and less than 8 times stronger at temperatures above 22.5°C (\(\sim 7.4\) at \(T = 40^\circ\)C). This consequently leads to a steeper or flatter slope between \(\delta^2\)H and \(\delta^{18}\)O and deviations from the GMWL. Furthermore, a third factor influencing the deuterium excess, which has not been extensively characterised yet, is the nonlinearity of the \(\delta\) scale. The strength of fractionation depends, apart from the fractionation factor, also on the \(\delta\) value itself. Since \(\delta^{18}\)O typically adopts higher values than \(\delta^2\)H, the same strength of fractionation at a given temperature has a larger effect on H\(^{18}\)\(_2\)O than on HD\(^{16}\)O when expressed in \(\delta\) notation. This nonlinear effect therefore leads to a less steep slope between \(\delta^2\)H and \(\delta^{18}\)O.

Thus, the deuterium excess can change even under pure equilibrium conditions, due to the temperature effect and the nonlinearity of the \(\delta\) scale. They usually have opposite signs and compensate each other to some extent, maintaining the linear relationship of the GMWL at cold temperatures (Craig, 1961; Gat, 1996). Nevertheless, very high deuterium excess values measured at high altitudes, e.g., in the Tien Shan mountains (Kreutz et al., 2003) or in the Andes (Samuels-Crow et al., 2014), indicate that nonequilibrium effects alone cannot explain the full deuterium excess variability. Thus, under very cold and depleted conditions, as at high latitudes or altitudes, the deuterium excess may lose some of its explanatory power. In this chapter, we evaluate separately the relative importance of the three factors (nonequilibrium effect, temperature effect, and nonlinearity of the \(\delta\) scale) on the deuterium excess in a simple Rayleigh model simulating the isotopic composition of air parcels during moist adiabatic ascent. Moreover, we propose and evaluate an alternative definition of the deuterium excess, which is based on a logarithmic scale, similar to the \(\delta^{17}\)O excess (Barkan and Luz, 2007), and is therefore unaffected by the nonlinear effect of the \(\delta\) scale.

### 3.2 Sensitivity experiments

We apply the Rayleigh model described in Section 2.1 with initial values of \(z_0 = 0\) km, \(p_0 = 1000\) hPa, \(T_0 = 20^\circ\)C and discretised height steps of \(\Delta z = 10\) m. The results are qualitatively very similar for different values of \(z_0, p_0, T_0\) and \(\Delta z\). The air parcels ascend until only 2% of their initial moisture remains (thus \(f = 0.02\)), which is at height \(z = 8.9\) km and pressure \(p = 317\) hPa. The initial \(\delta^2\)H in the air parcels (\(\delta^2\)\(_0\)) ranges from \(-300\%\) to \(0\%\), and the initial deuterium excess is set to \(0\%\). For quantifying the impact of the nonequilibrium
effect, temperature effect, and nonlinearity of the \( \delta \) scale on the deuterium excess, we perform three different sensitivity experiments with the fractionation factors \( \alpha^{2}H \) and \( \alpha^{18}O \):

- **Experiment A: standard fractionation factors with combined temperature and nonequilibrium effects**

  The fractionation factors consist of the temperature dependent equilibrium fractionation factors for liquid \( \alpha^{l/v}_{eq} \) (Majoube, 1971a) and ice \( \alpha^{l/v}_{eq} \) (Merlivat and Nief, 1967; Majoube, 1971b), and a nonequilibrium fractionation factor \( \alpha_{k} < 1 \) depending on the supersaturation with respect to ice \( S_{i} \) and the ratio of diffusion coefficients between the heavy and the light isotope \( D_{iso}/D \) (Jouzel and Merlivat, 1984; Blossey et al., 2010; cf. Equations 2.9 and 2.10).

  \[
  \alpha^{2}H = f_{l}^{c} \cdot \alpha^{2}H^{l/v}_{eq}(T) + f_{i}^{c} \cdot \alpha^{2}H^{l/v}_{eq}(T) \cdot \alpha^{2}H_{k} \tag{3.1}
  \]

  \[
  \alpha^{18}O = f_{l}^{c} \cdot \alpha^{18}O^{l/v}_{eq}(T) + f_{i}^{c} \cdot \alpha^{18}O^{l/v}_{eq}(T) \cdot \alpha^{18}O_{k} \tag{3.2}
  \]

  with \( \alpha_{k} = \frac{S_{i} \cdot D_{iso}/D}{\alpha^{l/v}_{eq} \cdot (S_{i} - 1) + \frac{D_{iso}}{D}} \tag{3.3} \)

  Thus, cloud formation involves a temperature effect and occurs under nonequilibrium conditions for \( T < 0^{\circ}C \). This definition of the fractionation factors is the most realistic version, and reveals changes of deuterium excess due to the nonlinearity of the \( \delta \) scale, the temperature effect, and the nonequilibrium effect in mixed phase and ice clouds.

- **Experiment B: fractionation factors dependent on temperature only**

  In this experiment, the nonequilibrium effect is switched off by setting the nonequilibrium fractionation factors \( \alpha_{k} = 1 \). The fractionation factors then consist of the equilibrium fractionation factors for liquid \( \alpha^{l/v}_{eq} \) and ice \( \alpha^{l/v}_{eq} \).

  \[
  \alpha^{2}H = f_{l}^{c} \cdot \alpha^{2}H^{l/v}_{eq}(T) + f_{i}^{c} \cdot \alpha^{2}H^{l/v}_{eq}(T) \tag{3.4}
  \]

  \[
  \alpha^{18}O = f_{l}^{c} \cdot \alpha^{18}O^{l/v}_{eq}(T) + f_{i}^{c} \cdot \alpha^{18}O^{l/v}_{eq}(T) \tag{3.5}
  \]

  Thus, cloud formation occurs under equilibrium conditions, but still involves a temperature effect. This definition reveals changes of deuterium excess due to the nonlinearity of the \( \delta \) scale and the temperature effect.
• **Experiment C: constant fractionation factors**

In this experiment, the temperature effect is switched off by using the equilibrium fractionation factor $\alpha^{2}{H}$ at $T_0 = 20{\, ^\circ C}$ during the entire ascent of the air parcels, and defining $\alpha^{18}{O}$ such that $(\alpha^{2}{H} - 1) - 8 \cdot (\alpha^{18}{O} - 1) = 0$.

\[
\alpha^{2}{H} = \alpha^{2}{H}_{eq}(T_0)
\]

\[
\alpha^{18}{O} = 8/(1/\alpha^{2}{H}_{eq}(T_0) + 7)
\]

Thus, cloud formation occurs under equilibrium conditions and without temperature effect. This definition reveals changes of deuterium excess due to the nonlinearity of the $\delta$ scale.

### 3.3 Deuterium excess in the air parcels

Figure 3.1 shows the evolution of the deuterium excess and the fractionation factors in the air parcels for the three experiments described in Section 3.2. $\alpha^{2}{H}_{ref}$ represents the value of $\alpha^{2}{H}$, for which (at the given $\alpha^{18}{O}$) the deuterium excess would be constant. It is defined such that:

\[
(f\alpha^{2}{H}_{ref}-1 \cdot R^2{H} - 1) - 8 \cdot (f\alpha^{18}{O}-1 \cdot R^{18}{O} - 1) = 0
\]

where $R' = R/R_{VSMOW}$. Thus, the difference between $\alpha^{2}{H}$ and $\alpha^{2}{H}_{ref}$ depicts changes in deuterium excess at each $f$. If $\alpha^{2}{H} > \alpha^{2}{H}_{ref}$ the deuterium excess decreases, if $\alpha^{2}{H} < \alpha^{2}{H}_{ref}$ it increases.

For all three experiments of the fractionation factors, the sign and magnitude of the deuterium excess in the remaining water vapour strongly depends on the initial $\delta^2{H}$ in the air parcels. With experiment A, the deuterium excess becomes negative for high $\delta^2{H}_0 (> -80{\, ^\circ _{oo}})$ (Figure 3.1 a, left), reflecting the nonequilibrium and temperature effect (both the faster diffusion of HD$^{16}{O}$ toward the ice crystals, and the more than 8 times stronger fractionation of HD$^{16}{O}$ at low temperatures lead to a negative deuterium excess in the remaining water vapour). For low $\delta^2{H}_0 (< -160{\, ^\circ _{oo}})$ the deuterium excess becomes positive and reaches values above $76{\, ^\circ _{oo}}$ for small fractions of remaining water vapour $f$. This can also be seen in the evolution of the fractionation factors (Figure 3.1 a, right). In most of the air parcels $\alpha^{2}{H}$ is lower than $\alpha^{2}{H}_{ref}$, meaning that the deuterium excess increases. The deactivation of the nonequilibrium effect leads to more positive deuterium excess values at low fractions of remaining water vapour, where temperatures are low (Figure 3.1 b, left). The fractionation factors
### 3.3 Deuterium Excess in the Air Parcels

#### 3.3.1 Evolution of the Standard Deuterium Excess for Different Initial $\delta^2$H (left) and the Fractionation Factors $\alpha^2$H (right) as a Function of the Fraction of Remaining Water Vapour in the Rayleigh Model for the Three Experiments of $\alpha$ Given in Section 3.2.

- **Experiment A:** temperature effect + nonequilibrium effect
  - $\delta^2$H$_0 = 0$‰
  - $\delta^2$H$_0 = –150$‰
  - $\delta^2$H$_0 = –300$‰

- **Experiment B:** temperature effect
  - $\delta^2$H$_0 = 0$‰

- **Experiment C:** constant $\alpha$
  - $\delta^2$H$_0 = 0$‰

#### Rayleigh model

The red lines show $\alpha^2$H, and the dark, medium and light blue lines show $\alpha^2$H$_{ref}$ for an initial $\delta^2$H of 0‰, –150‰ and –300‰, respectively. $\alpha^2$H$_{ref}$ is defined such that $$(f_{\alpha^2H_{ref}} - 1) \cdot R'_{2H-1} = 0.$$ It shows the value $\alpha^2$H would need to have in order to get $d = 0$‰. The two dashed black lines indicate the temperature range of mixed phase clouds.

---

**Figure 3.1:** Evolution of the standard deuterium excess for different initial $\delta^2$H (left) and the fractionation factors $\alpha^2$H (right) as a function of the fraction of remaining water vapour in the Rayleigh model for the three experiments of $\alpha$ given in Section 3.2. The red lines show $\alpha^2$H, and the dark, medium and light blue lines show $\alpha^2$H$_{ref}$ for an initial $\delta^2$H of 0‰, –150‰ and –300‰, respectively. $\alpha^2$H$_{ref}$ is defined such that $(f_{\alpha^2H_{ref}} - 1) \cdot R'_{2H-1} = 0$. It shows the value $\alpha^2$H would need to have in order to get $d = 0$‰. The two dashed black lines indicate the temperature range of mixed phase clouds.
increase faster and the gap between $\alpha^2 H$ and $\alpha^2 H_{ref}$ becomes larger (Figure 3.1 b, right). If neither the nonequilibrium nor the temperature effect are present the deuterium excess still becomes positive for almost all $\delta^2 H_0$ (Figure 3.1 c, left). Only the most enriched air parcels experience a small increase of deuterium excess in the beginning of the ascent (Figure 3.1 c, right). Hence, the large increase of the deuterium excess with the full definition of experiment A originates from the nonlinearity of the $\delta$ scale. In comparison, the nonequilibrium and temperature effect only have a minor impact on the deuterium excess.

This may be problematic for the common application of the deuterium excess as a proxy for the meteorological conditions at the moisture source. The application is based on the assumption that the deuterium excess is unaffected by equilibrium processes, e.g., rain formation, and therefore remains roughly constant during the transport of air parcels. As shown above, this assumption does not hold in depleted regimes, where possible initial deuterium excess values of $\delta \neq 0$ (caused by evaporation from the surface) are overwritten by the nonlinear effect of the $\delta$ scale. The origin of this effect can be explained mathematically with the Rayleigh condensation equation (Equation 1.5). Since the fractionation factor $\alpha$ is in the exponent of the equation, the relationship between $\ln(R')$ and $\ln(f)$ is linear for constant $\alpha$:

$$\frac{d \ln(R')}{d \ln(f)} = \alpha - 1$$

(3.9)

**Figure 3.2:** Regressions of (a) $\ln(R'^2 H)$ and $\ln(R'^{18} O)$ and (b) $\delta^2 H$ and $\delta^{18} O$ in the Rayleigh model with experiment C (constant $\alpha$) and an initial $\delta^2 H$ of $-100\%$. The grey shaded area in (b) indicates the deuterium excess as the difference between the simulated values and the black line fitting the equation $\delta^2 H = 8 \cdot \delta^{18} O$. 
Transformation from $\frac{d \ln (R')}{d \ln (f)}$ to $\frac{d \delta}{d \ln (f)}$ then imposes a nonlinear term to the equation (Gat, 1996):

$$
\frac{d \ln (R')}{d \ln (f)} = \frac{d \ln (\delta + 1)}{d \ln (f)} = \frac{1}{\delta + 1} \cdot \frac{d \delta}{d \ln (f)} = \alpha - 1 \tag{3.10}
$$

which means that the change of $\delta$ with $f$ depends on $\delta$ itself and therefore the relationship between $\delta^{2}H$ and $\delta^{18}O$ is nonlinear.

Figure 3.2 shows that the slope between $\ln (R'^{2}H)$ and $\ln (R'^{18}O)$ in the air parcels is constant for experiment C with constant $\alpha$ (Figure 3.2 a), while the slope between $\delta^{2}H$ and $\delta^{18}O$ changes with a decreasing fraction of remaining vapour (Figure 3.2 b). The vertical distance between the $\delta$ values in vapour and the line fitting the equation $\delta^{2}H = 8 \cdot \delta^{18}O$ (grey shading in Figure 3.2 b) corresponds to the deuterium excess in Figure 3.1 c (left).

### 3.4 An alternative definition of the deuterium excess

The large increase of deuterium excess due to the $\delta$ scale effect, together with the linear relationship between $\ln (R'^{2}H)$ and $\ln (R'^{18}O)$ in the Rayleigh model, suggest to test an alternative definition of the deuterium excess, which is based on the logarithmic scale. Such an approach has been used previously for the $\delta^{17}O$ excess, which is defined as $\ln (R'^{17}O) - 0.528 \cdot \ln (R'^{18}O)$ (Barkan and Luz, 2007). We propose an alternative definition of the deuterium excess that follows the same principle, but uses a ratio instead of the difference of the logarithms, similar to the definition of the $\delta$ values:

$$
\tilde{d} = \frac{R'^{2}H}{R'^{18}O^m} - 1 \quad (\text{in } \%_{oo}) \tag{3.11}
$$

The exponent $m$ is determined from the GNIP measurements (IAEA/WMO, 2016; see Chapter 1). Figure 3.3 shows the correlation of the annual mean values of $\ln (R'^{2}H)$ and $\ln (R'^{18}O)$ in the GNIP measurements between 1961 and 2014. They fall on a line with a slope of approximately 8.8, which means that $R'^{2}H \approx R'^{18}O^{8.8} \cdot e^{n}$, where $n$ is the intercept in logarithmic space. We therefore choose the value of $m = 8.8$ in Equation 3.11, and calculate $\tilde{d}$ for the air parcels in the Rayleigh model. Since it uses the exponential formulation, we hereafter refer to this definition as the exponential deuterium excess.
Figure 3.3: Regression of the annual mean \(\ln(R'_{2H})\) and \(\ln(R'_{18O})\) in the GNIP measurements during the years 1961–2014 for all stations which measured continuously during at least one year. Each dot represents one station and one year, and the colours indicate the latitude of the stations. \(r\) is the correlation, \(m\) and \(n\) are the slope and the intercept of the regression line (black line), respectively.

### 3.5 Exponential deuterium excess in the air parcels

Again we consider three experiments with differing fractionation factors, and a new experiment D instead of C, such that \(\frac{\alpha^2_{2H}}{\alpha^1_{18O}} - 1 = 0\):

- **Experiment D**: constant fractionation factors for the exponential deuterium excess

  \[\alpha^2_{2H} = \alpha^2_{2H}^{\text{eq}}(T_0)\]  
  \[\alpha^{18}_{18O} = \alpha^2_{2H}^{\text{eq}}(T_0)^{1/m}\]  

Experiments A and B are the same as in Section 3.2.

Figure 3.4 shows the evolution of the exponential deuterium excess and the fractionation factors in the air parcels. \(\alpha^2_{2H\text{ref}}\) is now defined such that:

\[\frac{\alpha^2_{2H\text{ref}}^{-1} \cdot R'_{2H}}{\left(\alpha^{18}_{18O}^{-1} \cdot R'_{18O}\right)^8} - 1 = 0\]  

(3.14)
Figure 3.4: Evolution of the exponential deuterium excess for different initial $\delta^2H$ (left) and the fractionation factors $\alpha^{2H}$ (right) as a function of the fraction of remaining water vapour in the Rayleigh model for the three experiments of $\alpha$ given in Section 3.2 and 3.5. The red lines show $\alpha^{2H}$, and the light blue lines show $\alpha^{2H}_{\text{ref}}$. $\alpha^{2H}_{\text{ref}}$ is defined such that $(f^{2H}_{\text{ref}} - 1) \cdot R^{2H} = (f^{18O} - 1) \cdot R^{18O} = 8.8$. It shows the value $\alpha^{2H}$ would need to have in order to get $\tilde{d} = 0\%^{\text{iso}}$ (independent of the initial $\delta^2H$). The two dashed black lines indicate the temperature range of mixed phase clouds.
If the nonequilibrium and temperature effect are included, the exponential deuterium excess becomes negative for small fractions of remaining vapour (Figure 3.4 a, left). The temperature effect alone leads to a negative deuterium excess as well (Figure 3.4 b, left). Most importantly, the deuterium excess does not depend on the initial $\delta^2$H, and is almost 0‰ if neither the nonequilibrium effect nor the temperature effect are present (Figure 3.4 c, left). This can also be seen in the difference between $\alpha^2H_{\text{ref}}$ and $\alpha^2H$, which has a constant value close to 0 during the entire ascent of the air parcels (independent of the initial $\delta^2$H) in experiment D (Figure 3.4 c, right). The temperature effect increases the distance between $\alpha^2H_{\text{ref}}$ and $\alpha^2H$ (Figure 3.4 b, right), and the nonequilibrium effect leads to a clear separation at low temperatures, indicating that the deuterium excess in the remaining water vapour decreases rapidly (Figure 3.4 a, right). Thus the exponential deuterium excess in the air parcels mainly reflects the nonequilibrium effect due to ice cloud formation, the temperature effect, and the initial signal from ocean or land evaporation.

The sensitivity of the deuterium excess to the moisture source conditions, namely relative humidity and sea surface temperature during evaporation from the ocean, can be estimated with the closure assumption by Merlivat and Jouzel (1979), which assumes that the only source of near-surface vapour over the ocean is evaporation from the same location. The exponential deuterium excess has a small offset of $\sim 5$‰ compared to the standard deuterium excess at 100% relative humidity and 20 °C (Figure 3.5), but otherwise the relations are similar to the standard deuterium excess, with a slightly stronger dependence on relative humidity (−6.4‰/10% compared to −5.6‰/10%). Therefore a similar signal due to ocean or land evaporation can be expected for both definitions.

**Figure 3.5:** Standard and exponential deuterium excess in the evaporation flux as a function of relative humidity and sea surface temperature, calculated with the closure assumption of Merlivat and Jouzel (1979) using the wind speed independent nonequilibrium fractionation factors from Pfahl and Wernli (2009).
3.6 Discussion

The Rayleigh model used here is a simplified representation of the atmospheric circulation, but nevertheless it points out an important aspect of deuterium excess variations. Many studies have found a negative correlation between the (standard) deuterium excess and $\delta^2$H (or $\delta^{18}$O) at high latitudes (e.g., Petit et al., 1991; Dahe et al., 1994; Vimeux et al., 1999; Uemura et al., 2004; Jouzel et al., 2007), which was often interpreted as a signal of stronger nonequilibrium fractionation at lower temperatures, the temperature effect, or different moisture origins (Masson-Delmotte et al., 2008).

Our Rayleigh model can reproduce the negative correlation between the standard deuterium excess and $\delta^2$H for every $f$ (except $f = 0$, Figure 3.6), even with the constant $\alpha$ scenario, hence, without nonequilibrium or temperature effect, and with a single initial deuterium excess value ($d = 0$). The steepness of the slope increases with smaller $f$, and the average over all $f$ has a parabolic shape, similar to, e.g., Petit et al. (1991).

We therefore argue that this correlation between deuterium excess and $\delta^2$H is to some extent an artefact of the deuterium excess definition and not necessarily related to a meteorological phenomenon. This is in agreement with recent studies by Risi et al. (2013) and Touzeau et al. (2016), who showed that, in Antarctica, the $^{17}$O excess, in contrast to the deuterium excess, is mostly positively correlated with $\delta^2$H, and that the nonlinear effect of the $\delta$ scale (termed Rayleigh effect and distillation effect, respectively, in their articles) can cause an increase of the deuterium excess with low $\delta^2$H.

![Figure 3.6](image)

*Figure 3.6*: Standard deuterium excess as a function of $\delta^2$H for different fractions of remaining water vapour $f$ in the Rayleigh model with experiment C (constant $\alpha$) from Section 3.2. The black line shows the weighted average over all $f$. 
This artificial increase of deuterium excess could be avoided by using the exponential definition (Equation 3.11), which resembles the $^{17}$O excess definition. As the $^{17}$O excess, the exponential deuterium excess is based on the logarithmic scale and therefore not affected by the nonlinearity of the $\delta$ scale. In our Rayleigh model it mainly reflects the nonequilibrium effect due to ice cloud formation and the temperature effect due to the temperature dependence of the equilibrium fractionation factors. While the nonequilibrium effect always decreases the exponential deuterium excess in the remaining water vapour, the temperature effect can work in both directions. Figure 3.7 shows the impact of a single Rayleigh condensation event with $f_{k+1}/f_k = 0.9$ under equilibrium conditions (experiment B from Section 3.2) on both deuterium excess definitions as a function of temperature. The sign of the exponential deuterium excess in the remaining vapour depends only on temperature, with negative values below and positive values above $\sim 17^\circ C$. The sign of the standard deuterium excess depends on temperature and on the $\delta$ values, due to the opposing effects of temperature and the nonlinearity of the $\delta$ scale. Note that for a range between $-160^\circ < \delta^2H < -80^\circ$ the two tend to cancel out (compensation range in Figure 3.7), which supports the hypothesis of Craig (1961) and Gat (1996), that the linear relationship between $\delta^2H$ and

**Figure 3.7**: The change of deuterium excess during a single Rayleigh condensation event with $f_{k+1}/f_k = 0.9$ under equilibrium conditions (experiment B in Section 3.2) as a function of temperature. The coloured lines show the standard deuterium excess for different $\delta^2H$, the black line shows the exponential deuterium excess. The two vertical dashed black lines indicate the temperature range of mixed phase clouds and the grey hatching depicts the compensation range (lines which cross the zero deuterium excess line).
δ\(^{18}\)O is sustained by the opposing effects, at least as long as the isotope ratios fall in the given range. This can also be seen in Figure 3.1 b (left), where the deuterium excess is constant in the beginning for \(-160^{\circ}\text{o} < \delta^{2}\text{H}_0 < -80^{\circ}\text{o}\). Nevertheless, for depleted air parcels with \(\delta^{2}\text{H} < -160^{\circ}\text{o}\) the nonlinear effect of the \(\delta\) scale is too large to be compensated by the temperature effect at any temperature between \(-30^\circ\text{C}\) and \(30^\circ\text{C}\). Over the whole depicted temperature and \(\delta^{2}\text{H}\) range the average temperature effect is smaller for the exponential than for the standard deuterium excess. This underlines that, by being independent of the \(\delta\) values, the exponential definition of the deuterium excess has a clear advantage compared to the standard definition for processes involving Rayleigh condensation.

However, isotopic variability is not only governed by Rayleigh condensation and evaporation in reality. One important process that is not accounted for in our model is the mixing of air parcels during transport, and the exponential deuterium excess, as well as the \({}^{17}\text{O}\) excess, have a drawback related to mixing (Risi et al., 2010b). Since the exponential deuterium excess is defined as a ratio, it is not conserved when two air parcels mix. Assuming air parcels 1 and 2 mix with a relative moisture fraction of \(p\) and \(q = 1 - p\), respectively, then the total deuterium excess of both air parcels \(\tilde{d}_{\text{mix}}\) is:

\[
\tilde{d}_{\text{mix}} = \frac{p \cdot R'_{2\text{H}1} + q \cdot R'_{2\text{H}2}}{(p \cdot R'_{18\text{O}1} + q \cdot R'_{18\text{O}2})^m} - 1 \tag{3.15}
\]

In contrast, the linearly combined deuterium excess of the two air parcels \(\tilde{d}_{\text{lin}}\) would be:

\[
\tilde{d}_{\text{lin}} = \frac{p \cdot R'_{2\text{H}1}}{R'_{18\text{O}1}^m} + \frac{q \cdot R'_{2\text{H}2}}{R'_{18\text{O}2}^m} - 1 \tag{3.16}
\]

The total deuterium excess of both air parcels \(\tilde{d}_{\text{mix}}\) can be larger or smaller than the linear combination \(\tilde{d}_{\text{lin}}\), depending on the isotope ratios in the individual air parcels (more details are given in Appendix A.2). Figure 3.8 shows the difference between \(\tilde{d}_{\text{mix}}\) and \(\tilde{d}_{\text{lin}}\) as a function of the difference between the two air parcels’ \(\delta^{2}\text{H}\) and \(\delta^{18}\text{O}\) for \(p = q = 0.5\). Here the first air parcel’s \(\delta^{2}\text{H}\) and \(\delta^{18}\text{O}\) are set to \(-80^{\circ}\text{o}\) and \(-10^{\circ}\text{o}\), respectively, while the second air parcel’s \(\delta^{2}\text{H}\) and \(\delta^{18}\text{O}\) vary from \(-160^{\circ}\text{o}\) to \(0^{\circ}\text{o}\) and from \(-20^{\circ}\text{o}\) to \(0^{\circ}\text{o}\), respectively. The largest difference occurs if the deuterium excess of the two air parcels is strongly different (upper left and lower right corner in Figure 3.8), or if one air parcel is very enriched and the other is very depleted, but both have a small deuterium excess (lower left and upper right corner in Figure 3.8). The result does not depend much on the different absolute values of \(\delta^{2}\text{H}\) and \(\delta^{18}\text{O}\) in the air parcels, as can be deduced from the almost point symmetry of Figure 3.8.
Figure 3.8: Difference between $\tilde{d}_{\text{mix}}$ and $\tilde{d}_{\text{lin}}$ for different values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in air parcels 1 and 2. The solid black lines show the difference of the deuterium excess in the air parcels ($\tilde{d}_2 - \tilde{d}_1$). The dashed black lines indicate where $\tilde{d}_{\text{mix}} = \tilde{d}_{\text{lin}}$. Note the nonlinear colour scale.

This mixing problem is a disadvantage of the logarithmic definition affecting both the exponential deuterium excess and the $^{17}\text{O}$ excess, but not the standard deuterium excess (due to its linear definition). The effect seems rather small for one single mixing event, but the accumulated impact is unclear. For the $^{17}\text{O}$ excess in Antarctic precipitation, Risi et al. (2010b) estimated the role of mixing to be secondary, explaining at most 35% of the observed variability. We assume that this would be similar for the exponential deuterium excess. However, it is difficult to assess this on the global scale, and further investigations are needed.

In view of these points, abandoning the standard deuterium excess definition would not be appropriate, especially when dealing with enriched to moderately depleted air masses, for which the temperature effect and the nonlinear effect of the $\delta$ scale are either small or cancel out. We nevertheless suggest to additionally consider the exponential deuterium excess definition especially at high latitudes or altitudes, where moisture is very depleted and therefore the nonlinear effect of the $\delta$ scale can be large.

### 3.7 Conclusions

This chapter has evaluated the influence of the nonequilibrium effect, the temperature effect, and the nonlinearity of the $\delta$ scale on the deuterium excess in a simple Rayleigh model simulating the isotopic composition of air parcels during moist adiabatic ascent. We found that, for small fractions of remaining vapour, the standard deuterium excess...
in the remaining water vapour can reach very high values even under equilibrium conditions and without temperature effect, depending on the initial $\delta$ values. This is due to the nonlinearity of the $\delta$ scale, which implies that the change of $\delta$ depends on $\delta$ itself, and therefore the air parcels’ trajectories in the $\delta^2H – \delta^{18}O$ phase space are curved, with a slope flatter than 8 for depleted values.

We tested an alternative definition of deuterium excess (the exponential deuterium excess) that is based on the logarithmic scale, and therefore not affected by the nonlinearity of the $\delta$ scale. This exponential deuterium excess is almost constant if condensation occurs under equilibrium conditions and without temperature effect, and it is independent of the initial $\delta$ values. The temperature effect can lead to more negative or more positive exponential deuterium excess values in the remaining vapour, depending on the temperature in the air parcels, while the nonequilibrium effect during ice and mixed phase cloud formation always leads to more negative values, due to the faster diffusion of HD$^{16}$O to the ice crystals.

A disadvantage of the exponential deuterium excess is that, in contrast to the standard deuterium excess, it is not conserved during mixing, since it is defined as a ratio instead of a difference. This can lead to changes of deuterium excess without phase transitions, depending on the $\delta$ values.

In summary, there is no perfect deuterium excess definition, which would be a pure measure for nonequilibrium effects, and independent of the background isotope ratios. According to the location and purpose, the standard or the exponential definition might be more suitable. However, since they have different benefits and deficiencies, it may in many cases be helpful to use both.
Chapter 4

Variations of $\delta^2$H in an idealised extratropical cyclone


4.1 Introduction

Extratropical cyclones can strongly influence isotopic variability on synoptic time scales. Many studies found that during cold front passages heavy isotopes in water vapour and precipitation decrease notably. This decrease has been attributed to several processes, including (i) the arrival of new and colder air masses behind the front (e.g., Gedzelman and Lawrence, 1990), (ii) formation of clouds at different heights (e.g., Rindsberger et al., 1990), (iii) progressive depletion during rainout (e.g., CellJeanton et al., 2004), or (iv) changes in below cloud interactions (e.g., Aemisegger et al., 2015) (see Section 1.2.2 and Appendix B.1 for more details). However, although these processes are all known to influence isotopic variations in an extratropical cyclone, their relative importance has not yet been thoroughly quantified.

For this purpose numerical models can be helpful, since they provide the full structure of the isotope fields and can be applied for sensitivity studies to identify relevant mechanisms that influence the isotopic composition of water vapour and precipitation. In this chapter we use COSMOiso (Pfahl et al., 2012; see Section 2.2) in an idealised baroclinic channel framework to investigate stable water isotopes in an isolated extratropical cyclone. Thanks to its advanced microphysical scheme and nonhydrostatic numerics, COSMOiso is a very suitable model for simulating mesoscale weather systems and their associated isotopic changes at high spatial and temporal resolutions. The idealised framework is a classical and fruitful approach to study extratropical cyclones (e.g., Hoskins and West, 1979; Wernli et al., 1998). With the help of several
experiments with altered isotopic setup we are able to quantify the influence of specific 
processes on the isotopic composition of water vapour and precipitation in the cyclone. 
In particular, we focus on the cold front and disentangle the processes (i – iv) that lead 
to the commonly observed decrease of the isotope ratio during its passage.

4.2 Model and experiments

4.2.1 Dynamical setup

We use COSMOiso in an idealised baroclinic channel setup (Schemm et al., 2013) 
on an $f$-plane centred at 45°N (with a constant Coriolis parameter $f = 1.03 \cdot 10^{-4}$ s$^{-1}$) 
to simulate stable water isotopes in an isolated extratropical cyclone. The model do- 
main covers 16800 km × 8400 km × 12 km with a resolution of 21 km and 200 m in 
the horizontal and vertical, respectively, and is situated entirely over the ocean. The 
boundaries are periodic in the zonal direction and relaxed towards the initial conditions 
in the south and north as well as at the model top (following Davies, 1976).
The channel’s basic state consists of a zonally uniform jet stream ($u_{\text{max}} = 45$ ms$^{-1}$) in 
thermal wind balance (Figure 4.1) and a relative humidity profile decreasing linearly 
with height ($\text{RH} = 80\%$ at $z = 0$). Temperature decreases (nonlinearly) with latitude 
and height ($\bar{T} = 7.3^\circ$C at $z = 0$). To trigger the formation of the cyclone a localised 
positive potential vorticity perturbation is added near the tropopause at 8 km altitude. 
Radiation and surface friction are turned off.

4.2.2 Isotope experiments

Four main experiments are performed to decompose the total isotopic signal of the 
cyclone into contributions from separate processes (i – iv, see Section 4.1). They have 
identical dynamics, but differ in their initial isotopic composition of water vapour and 
in the parameterisation of fractionation. Experiment 1a (“fractionation”, Figure 4.1 a), 
has a uniform initial $\delta^2$H and fractionation is switched on for all phase transitions in the 
atmosphere. This experiment includes processes iii (progressive depletion during rain- 
out), and iv (changes in below cloud interactions), but – because of the uniform initial 
$\delta^2$H field – is not affected by processes i (arrival of new air masses) and ii (formation 
of clouds at different heights). In contrast, experiments 2 and 3 (“vertical transport”, 
Figure 4.1 b, and “horizontal transport”, Figure 4.1 c) have a vertical and horizontal 
gradient of initial $\delta^2$H, proportional to the mean vertical and horizontal temperature 
gradient, respectively (see Appendix B.2), and fractionation is switched off, meaning 
that the isotope ratios remain constant during all phase transitions and the stable water 
isotopes are purely passive tracers. These two experiments include only processes ii
4.3 Results

4.3.1 Cyclone evolution

The initial potential vorticity perturbation grows into a mature extratropical cyclone with a sea level pressure minimum of 949 hPa after 4.5 days of simulation time. Figure 4.2 shows two pseudo satellite images of the cyclone, whose life cycle closely resembles the Shapiro-Keyser model (Shapiro and Keyser, 1990): the cold and warm front separate and build a so-called T-bone structure with the cold front almost perpendicular
Figure 4.2: Pseudo satellite images of the idealised extratropical cyclone 4.5 days after the start of the simulation. (a) Visible channel with vertically integrated liquid and ice cloud content in gm⁻² (shaded), sea level pressure in hPa (white lines) and the 3 mm isoline of 12 h accumulated precipitation (yellow line). The cold front (purple) and warm front (red) are identified at 850 hPa with the front detection algorithm by Jenkner et al. (2010). The green crosses indicate the southernmost, central and northernmost location of the observation sites. (b) Infrared channel with cloud top temperature in °C (shaded) and equivalent potential temperature at 3.1 km height in K (lines). In cloud-free regions the temperature represents the temperature on the lowest model level.

Most of the clouds form along the cyclone’s cold front and in the northern part of its warm sector (Figure 4.2a). The cold sector is covered by shallow convective clouds, while over the warm sector clouds that have formed in the warm conveyor belt (e.g., Browning et al., 1973; Carlson, 1980; Schemm et al., 2013) reach very high levels and cold cloud top temperatures (Figure 4.2b). Another band of lower and warmer clouds stretches along the bent-back front to the north of the cyclone centre. Precipitation falls mainly at the cold front and the bent-back front with a maximum of 29 mm in 6 hours.

4.3.2 Stable water isotopes in water vapour

When clouds form, isotopic fractionation removes heavy isotopes from the water vapour. This effect is clearly visible in the pattern of the simulation “fractionation” (Figure 4.3a), which started with a uniform $\delta^2H = -80^\permil$ and reached $\delta^2H < -170^\permil$ in some areas after 4.5 days. The depletion is strongest in the cold sector and along the warm front, which indicates that microphysical processes have been most active.
4.3 Results

Figure 4.3: $\delta^2$H in water vapour at 3.1 km for (a, b, c) the three separate simulations, (d) their sum, (e) the reference, and (f) the difference between the sum and the reference. The solid black lines show sea level pressure in hPa and the dashed dark blue line is the 80% isoline of relative humidity. Note the different colour scale for (f).

there. Note that the $\delta^2$H pattern is an integrated view on the air parcels’ fractionation history, showing the accumulated depletion since the start of the simulation.

In the simulations “vertical transport” and “horizontal transport” (Figs. 4.3 b,c) the isotopes are passive tracers and therefore provide information about transport of moisture in the baroclinic wave. They show at which height and latitude the air parcels were located at the beginning of the simulation. In the “vertical transport” simulation the ageostrophic circulation at the fronts brings depleted moisture from higher levels to the cold side and enriched moisture from lower levels to the warm side. This leads to a considerable gradient of $\delta^2$H across the fronts, which is sharpest at the cold front and in the wrapped-up part of the bent-back front ($\Delta \delta^2$H/$\Delta x \approx 50^{\circ}\text{o} / 100 \text{ km at the cold front}$). In the “horizontal transport” simulation the geostrophic circulation of the cyclone advects depleted moisture from the north in the cold sector and enriched moisture from the south in the warm sector, also leading to a substantial gradient of $\delta^2$H across both fronts with the same sign as in the “vertical transport” simulation ($\Delta \delta^2$H/$\Delta x \approx 45^{\circ}\text{o} / 100 \text{ km at the cold front}$).

The sum (Figure 4.3 d) is defined as “fractionation” + “vertical transport” + “horizontal transport” + 2 $\cdot$ 80$^{\circ}\text{o}$, where the term 2 $\cdot$ 80$^{\circ}\text{o}$ compensates the offset of $\delta^2$H = –80$^{\circ}\text{o}$ at the surface and at 45$^\circ$N in the “vertical transport” and “horizontal transport” simulation, respectively. It is very close to the “reference” simulation (Figure 4.3 e), with high $\delta^2$H between –150$^{\circ}\text{o}$ and –50$^{\circ}\text{o}$ in the warm sector and low $\delta^2$H between –250$^{\circ}\text{o}$.
4.3.3 Stable water isotopes in surface precipitation

The isotope ratio in surface precipitation is in general more enriched than the (initial) isotopic composition of vapour, because the heavy isotopes preferentially go to the liquid or solid phase. In the simulation “fractionation” $\delta^2$H in precipitation is $>-20\%$ over wide areas (Figure 4.4 a). Only in the northern part of the warm sector values are very low ($<-125\%$), which is likely caused by the continuous depletion through condensation in the cyclone’s warm conveyor belt. Interestingly precipitation is more enriched along the cold front in the south than at the bent-back front in the north of the domain while fractionation is supposedly stronger in the north due to lower temperatures. This illustrates the difference in the isotopic nature of rain and snow (south and north of the $0^\circ$C line in Figure 4.4, respectively): rain equilibrates its isotopic composition with the surrounding water vapour and experiences fractionation when it evaporates. Snow in contrast carries its (depleted) signal from where it formed all the way down to the surface (Jouzel and Merlivat, 1984). Therefore rain is typically more enriched when it reaches the surface compared to snow. In simulation 1b without below cloud interactions this north-south difference disappears (see Appendix B.5).

In the simulations “vertical transport” and “horizontal transport” (Figs. 4.4 b,c) clouds and precipitation directly adopt the isotope ratio of the vapour from which they form, without any fractionation. The $\delta^2$H values in surface precipitation therefore indicate the height and latitude of the cloud formation. $\delta^2$H in the “vertical transport” simulation is rather uniform. It varies mainly between $-125\%$ and $-95\%$ and there is no north-south gradient, hence most precipitation formed at a similar height (between 1 km and 2 km, as indicated by Figure 4.1 b). In the “horizontal transport” simulation the pattern of $\delta^2$H in precipitation is related to the pattern in water vapour (Figure 4.3 c) with enriched values in the warm sector and depleted values in the cold sector, resulting
Figure 4.4: $\delta^2$H in surface precipitation for (a, b, c) the three separate simulations, (d) their sum, (e) the reference, and (f) the difference between the sum and the reference. The solid black lines show sea level pressure in hPa and the dashed line is the 0°C isoline of temperature at the lowest model level. Note the different colour scale for (f).

in a strong contrast of $\delta^2$H in precipitation between the cold front and the cold sector shallow convection.

For precipitation, the sum (Figure 4.4 d) and the “reference” simulation (Figure 4.4 e) differ more significantly than for vapour. The sum is too depleted in the warm sector and too enriched in the cold sector and to the north of the cyclone centre (Figure 4.4 f).

Nevertheless it is able to reproduce the overall pattern in the reference simulation, with relatively high $\delta^2$H between +10 $^\circ/_{^0}$/oo and +50 $^\circ/_{^0}$/oo in the cold frontal precipitation and lower $\delta^2$H between −80 $^\circ/_{^0}$/oo and −20 $^\circ/_{^0}$/oo in the cold sector shallow convection and in the precipitation at the bent-back front. Similar as in vapour (Section 4.3.2), horizontal transport determines the large-scale pattern of $\delta^2$H in precipitation with the contrast between the warm and the cold sector. Vertical transport leads to a nearly uniform depletion of the precipitation with a minimum at the bent-back front, which is also visible in the sum. In and below cloud fractionation adds the north-south gradient to the $\delta^2$H values, as well as the minimum in the northern part of the warm sector.

4.3.4 Frontal passage

Time series are now considered at grid points that are passed by the cold front after 4.5 days (green crosses in Figure 4.2 a). They reflect the temporal evolution of stable water isotopes in vapour and rain, and of temperature, relative humidity and rain amount. At the surface, evaporation from the ocean brings the air close to saturation,
and the $\delta^2H$ values only show a gradual depletion due to the change of air masses (not shown). More interestingly, at higher levels (between 1.9 km and 2.7 km, see also Appendix B.6) $\delta^2H$ in vapour experiences a drop of $\sim -41^{\circ}O$ at the time of the pre-frontal precipitation maximum (Figure 4.5), followed by a short increase and a second drop of $\sim -109^{\circ}O$ concurrent with the decrease in temperature and relative humidity. Since the sum is very close to the “reference” simulation in vapour, the observed time series can be decomposed into the three separate time series. Fractionation is to a large extent responsible for the first drop of $\delta^2H$, contributing $\sim -25^{\circ}O$, and vertical transport leads to an additional decrease of $\sim -16^{\circ}O$. The second drop is driven by horizontal transport, with $\sim -57^{\circ}O$, and vertical transport, with $\sim -48^{\circ}O$, and is therefore only due to the change of air masses.

The $\delta^2H$ values in the falling rain (also between 1.9 km and 2.7 km) show a similar trend as in the vapour with a decrease of $\sim -50^{\circ}O$ at the time of the precipitation maximum. Here the sum does not fully explain the reference, as it is too low before
and too high after the passage of the cold front. Nevertheless it shows a decrease, which is entirely caused by fractionation. Horizontal and vertical transport leave the values nearly unaffected. When additionally fractionation during rain evaporation and rain equilibration is deactivated, the decrease of $\delta^2$H gets weaker in the vapour yet stronger in the rain. This implies that below cloud microphysical interactions of vapour and rain are the main reason for the decrease of $\delta^2$H in vapour, while they partly compensate the decrease of $\delta^2$H in rain.

4.4 Discussion

4.4.1 Frontal passage

The trend of $\delta^2$H during the cold frontal passage in our simulation is a combination of two trends that have been observed in previous studies: the V-shaped trend (in vapour and rain) (e.g., Rindsberger et al., 1990; Celle-Jeanton et al., 2004; Aemisegger et al., 2015) and the descending trend (only in vapour) (e.g., Gedzelman and Lawrence, 1990; Pfahl et al., 2012). Thanks to the separate idealised simulations we can now determine which of the processes (i – iv) are responsible for these trends.

• The arrival of new air masses (process i) is visible in the simulations “horizontal transport” and “vertical transport”, where it leads to the second large drop of $\delta^2$H in water vapour. This process is clearly the dominant factor for the overall descending trend of $\delta^2$H during the cold front passage.

• The formation of clouds at different heights (process ii) is visible in precipitation in the “vertical transport” simulation. It leads to a slight increase of $\delta^2$H, meaning that the clouds formed from moisture that originated at lower levels. However, the effect is rather small.

• Progressive depletion during rainout (process iii) most likely causes the decrease of $\delta^2$H in precipitation, since it appears in both “fractionation” simulations. In vapour between 1.9 km and 2.7 km $\delta^2$H is nearly unaffected by this process, which means that the precipitation mainly formed at higher levels.

• Below cloud interactions (process iv) lead to lower $\delta^2$H values in vapour and higher $\delta^2$H values in rain. This is due to evaporation and equilibration of falling rain, whereby the isotopic signal of the rain is imprinted on the vapour, and vice versa. The effect on vapour is largest when the rain is most intense, whereas the effect on rain is largest when the relative humidity is low and evaporation is strong.
Hence, the V-shaped trend in precipitation during the cold frontal passage in our simulation is a combined signal for progressive depletion during rainout (decreasing branch) and below cloud interactions (increasing branch). This has already been suggested by Celle-Jeanton et al. (2004) as a possible explanation for their observations. The V-shaped trend in vapour is a signal for below cloud interactions, showing the imprint of the falling rain on the vapour, as in Aemisegger et al. (2015). Finally, the descending trend of $\delta^2H$ in vapour is a signal for the arrival of new air masses and is related to the classical temperature effect (Dansgaard, 1964). The formation of clouds at different heights plays only a minor role.

### 4.4.2 Nonlinearities

In regions, where the sum of the three separate simulations differs from the reference, nonlinearities of isotopic fractionation are important, meaning that the change in $\delta^2H$ depends on $\delta^2H$ itself. Surprisingly these nonlinearities are rather small for both vapour and precipitation, and therefore the three separate simulations are able to explain the $\delta^2H$ in the “reference” simulation. Still nonlinearities occur at some locations due to two main causes (for more details see Appendix B.7):

1. The $\delta$ scale is nonlinear, such that fractionation has a relatively larger effect on higher $\delta$ values (see Chapter 3). Therefore, for higher initial $\delta^2H$, water vapour becomes more depleted and condensate more enriched.

2. The enrichment of rain through evaporation and equilibration depends negatively on the vertical gradient of $\delta^2H$ in vapour ($\partial(\delta^2H)/\partial z$). Therefore, for more negative (positive) vertical gradients, rain becomes more enriched (depleted).

It is difficult to quantify the role of these effects for the minor nonlinearities observed in our simulations. Nevertheless we can speculate that effect (1) caused the overestimation of the sum in the precipitation north of the cyclone and in the cold sector, where temperatures are low and the $\delta^2H$ values differ most between the “fractionation” and the “reference” simulation. Effect (2) is likely responsible for the underestimation of the sum in the cold frontal precipitation, due to the negative vertical $\delta^2H$ gradient in the “reference” simulation.

### 4.5 Conclusions

This chapter has investigated the processes that influence the patterns and trends of $\delta^2H$ in an idealised extratropical cyclone. We used the isotope-enabled version of the COSMO model in a baroclinic channel framework with four different setups for the
isotopes, which allow isolating the effects of isotopic fractionation and vertical and horizontal transport. We found that nonlinear effects of fractionation on $\delta^2H$ are small, meaning that the isotopic signal can be decomposed into the signals from the three processes, and their relative importance for the isotopic variations in the cyclone can be evaluated quantitatively.

Horizontal transport determines the large-scale pattern of $\delta^2H$, leading to enriched values in the warm sector and depleted values in the cold sector. Vertical transport and fractionation are important near the fronts. In precipitation the V-shaped signal of $\delta^2H$ during the passage of the cold front is purely due to fractionation, caused by progressive depletion with increasing rainout and below cloud interactions between vapour and rain. In vapour $\delta^2H$ shows a combined V-shaped signal and a descending trend, which are caused by below cloud interactions and the arrival of more depleted air masses, respectively.

We would like to emphasise that this idealised cyclone and its effects on stable water isotopes may be representative for many, but not necessarily for all extratropical cyclones. Nevertheless the findings shed new light upon how these weather systems influence the variability of stable water isotopes in water vapour and precipitation, and may support future interpretations of isotope measurements during similar events.
Chapter 5

The influence of weather systems on seasonal isotopic variability

5.1 Introduction

When Dansgaard analysed the GNIP measurements in 1964, he found two meteorological variables that explained a large part of the monthly $\delta^2$H and $\delta^{18}$O variations in global precipitation (Dansgaard, 1964). The first was temperature, which was positively correlated with $\delta^2$H and $\delta^{18}$O, the second was precipitation amount, which was negatively correlated with $\delta^2$H and $\delta^{18}$O. Dansgaard named these two effects the temperature and amount effect and explained them with a simple Rayleigh model simulating rain formation in cooling air parcels. According to the Rayleigh condensation equation (Equation 1.5) water vapour and newly forming precipitation become progressively depleted with increasing rainout. This leads to a negative correlation of $\delta^2$H and $\delta^{18}$O with precipitation amount, and, since temperature controls the saturation vapour pressure and consequently the rainout of air parcels, a positive correlation of $\delta^2$H and $\delta^{18}$O with temperature. Additionally, heavy rain experiences less enrichment by below cloud interactions than light rain, due to the larger rain drop size and higher relative humidity (as discussed in Chapter 4). The temperature and amount effect led to the formulation of four second-order isotope effects: (1) the latitude effect, with lower $\delta$ values at higher latitudes, (2) the seasonal effect, with higher $\delta$ values in warm or dry seasons than in cold or wet seasons, (3) the continental effect, with lower $\delta$ values further away from the coast, and (4) the altitude effect, with lower $\delta$ values at higher altitudes. These effects characterise the mean isotopic composition of global precipitation and became widely used for the interpretation of stable water isotope measurements. However, on short time scales considerable variations occur, which can override the isotope effects, for example due to changes in transport patterns, precipitation-evapotranspiration rates, or moisture source conditions (Rozanski et al., 1982).
The last are commonly studied using the deuterium excess ($d = \delta^2H - 8 \cdot \delta^{18}O$; Dansgaard, 1964), as it is primarily governed by nonequilibrium fractionation during evaporation from the ocean (Craig and Gordon, 1965) and, at least partially, preserved during subsequent transport of air parcels (e.g., Armengaud et al., 1998), given that rainout is limited (see Chapter 3). According to the linear resistance model introduced by Craig and Gordon (1965) (Equation 2.11) the deuterium excess in the evaporation flux depends mainly on three meteorological variables: relative humidity with respect to the sea surface temperature, sea surface temperature, and, to some degree, wind speed. While relative humidity is a direct factor of influence in the Craig-Gordon model, sea surface temperature and wind speed affect the deuterium excess indirectly through the equilibrium and nonequilibrium fractionation factors ($\alpha_{eq}/\nu$ and $\alpha_k$), respectively.

The impacts of relative humidity, sea surface temperature and wind speed on deuterium excess are still under debate. Many studies interpreted deuterium excess as a proxy for sea surface temperature at the moisture sources (e.g., Barlow et al., 1993; Vimeux et al., 1999; Stenni et al., 2001; Uemura et al., 2012), neglecting its dependence on relative humidity. This was usually justified by the decreasing imprint of source relative humidity when moving away from the source as shown by simple Rayleigh models (e.g., Petit et al., 1991), the weak changes of relative humidity during glacial-interglacial cycles (e.g., Bush and Philander, 1999), and the negative correlation between sea surface temperature and relative humidity found in GCMs (e.g., Vimeux et al., 2001), which was used to include the dependence of deuterium excess on relative humidity in its dependence on sea surface temperature. However, according to Pfahl and Niedermann (2011) there is no systematic negative correlation between sea surface temperature and relative humidity in observations, and Pfahl and Sodemann (2014) found only very weak correlation between sea surface temperature and deuterium excess in present-day climate. Using a linear empirical model they showed that the strong relation between relative humidity at the moisture source and deuterium excess observed on daily time scales (Gat et al., 2003; Angert et al., 2008; Uemura et al., 2008; Pfahl and Wernli, 2008) also explains the seasonal cycle of deuterium excess in precipitation and should be taken into account when interpreting paleoclimatic variations of deuterium excess. This conclusion was supported by Steen-Larsen et al. (2014), who measured isotopes during 500 days on the Bermuda Islands and found a strong negative correlation between relative humidity and deuterium excess on daily to seasonal time scales. Apart from that, Pfahl and Wernli (2009) suggested that, unlike previously thought, wind speed may not have a significant influence on deuterium excess, since a constant nonequilibrium fractionation factor ($\alpha_k$) in the Craig-Gordon model led to a better representation of measured
daily deuterium excess variations than its classical formulation as a function of wind speed by Merlivat and Jouzel (1979), which was based on wind-tunnel experiments. The small influence of wind speed on deuterium excess was supported by observations over the South Indian and Southern Oceans (Uemura et al., 2010), and on the Bermuda Islands (Steen-Larsen et al., 2014). On the other hand, Benetti et al. (2014) observed variations in deuterium excess related to changes in the wind regime over the subtropical eastern North Atlantic. Hence, the exact dependence of $\delta^2$H, $\delta^{18}$O and deuterium excess on processes occurring on the daily time scale, and how this translates to longer term variations on seasonal to interannual time scales is still relatively unknown. This chapter aims at resolving some of the remaining uncertainties by providing a quantitative analysis of the processes responsible for isotopic variations on the daily to yearly time scale in a 10-year high resolution simulation of stable water isotopes over Europe. Thereby we focus on the following questions:

1. Which meteorological variables control the daily, monthly and yearly variability of $\delta^2$H and deuterium excess in Europe?

2. Which processes contribute most to the isotopic composition of air parcels and how do they influence isotopic variability?

3. What is the climatological imprint of weather systems on the isotopic composition of near-surface water vapour?

As a first step, COSMOiso simulations (see Section 2.2) with different isotope parameterisations and input data are compared and validated against GNIP measurements from IAEA/WMO (2016). The setup producing the best results is then used for the further analysis. To determine the relation between meteorological variables and isotopes, linear correlations are calculated at every grid point and on different time scales. Thereby, in addition to the Eulerian perspective, a Lagrangian perspective is adopted which follows individual trajectories. Subsequently, the trajectories are used to quantify the impact of particular processes and weather systems (extratropical cyclones and fronts) on isotopic variations.

5.2 Methods

5.2.1 Simulations

The simulations are run for the years 2002–2011 in a model domain covering most of Europe, as well as parts of North Africa and the North Atlantic (Figure 5.1). The resolution is 0.25° in the horizontal and between 16 m and 2808 m in the vertical, with 40
model levels. The model runs freely within the domain. For evaluating the performance of COSMOiso and its input data and parameterisations, we run six simulations in total, which differ in their initial and boundary data (ERAinterim/IsoGSM and ECHAMwiso) and in the parameterisation of isotopes in the soil model (S0: external, and S3: TERRAiso) and isotopic fractionation during ocean evaporation (E1: classical, and E2: wind speed independent). In the following, the different options are explained in more detail.

Input data

Initial and boundary data are provided by either IsoGSM (for the isotopes) together with ERAinterim (for the remaining atmospheric and surface fields) or ECHAMwiso. IsoGSM (Yoshimura et al., 2008) and ECHAMwiso (Werner et al., 2011) are isotope-enabled GCMs, which have been employed for nudged historical isotope simulations by Yoshimura et al. (2008), and Butzin et al. (2014), respectively. IsoGSM data are available every 6 hours at T62 spectral resolution and 17 vertical levels, with one additional soil level. ECHAMwiso data are available every 12 hours at T106 spectral resolution and 31 vertical levels, with two soil levels. Due to the coarse resolution of IsoGSM, the standard atmospheric and surface fields of the COSMOiso simulations using IsoGSM for the isotopes are forced at the lateral boundaries by ERAinterim re-

![Figure 5.1: Model domain of the COSMOiso simulations, shown by the black line. The GNIP stations of Valentia, Grimsel and Athens-Penteli are indicated by the green, blue and red marker, respectively.](image-url)
analyses (Dee et al., 2011) from the European Centre for Medium-Range Weather Forecasts (ECMWF), which are available every 6 hours at T255 spectral resolution and on 60 vertical levels (see also Pfahl et al., 2012). These simulations also assume a constant ocean isotope ratio of $\delta^{18}O = \delta^2H = 0^\circ$, while the others take the ocean values from ECHAMwiso.

**Land evaporation**

The isotope content of soil is either prescribed by external data (the soil isotope content of IsoGSM or ECHAMwiso) or coupled to COSMOiso through the prognostic isotope soil model TERRAiso (see Section 2.3). In the case of external data (S0) the model assumes that evaporation from land always occurs without fractionation. TERRAiso (S3), in contrast, distinguishes between different types of evaporation (e.g., bare soil evaporation or plant transpiration) involving different strengths of fractionation. Furthermore the coupling of TERRAiso and COSMOiso allows for feedbacks between the isotopes in the soil and in the atmosphere, which is not possible with prescribed soil data.

**Ocean evaporation**

The parameterisations of ocean evaporation differ in the definition of the nonequilibrium fractionation factor $\alpha_k$ in the Craig-Gordon equation (Equation 2.11). In the classical formulation (E1) from Merlivat and Jouzel (1979) $\alpha_k$ is a function of wind speed,

![Figure 5.2](image.png)

**Figure 5.2:** Nonequilibrium fractionation factor for $\text{H}_2^{18}$O $(1 - \alpha^{18}O_k$, in $\%)$ from Merlivat and Jouzel (1979) (red lines), and Pfahl and Wernli (2009) (blue line) as a function of 10 m wind speed (adapted from Pfahl and Wernli, 2009).
with a discontinuity at $\sim 7 \text{ m s}^{-1}$ (Figure 5.2, red lines). The revised version of $\alpha_k$ (E2) by Pfahl and Wernli (2009) uses a wind speed independent value, which is smaller (meaning stronger fractionation) than the classical formulation (Figure 5.2, blue line). IsoGSM and ECHAMwiso both use the classical formulation.

**Set up**

Hence we have the following set of simulations:

1. S0 E2 IsoGSM
2. S0 E1 IsoGSM
3. S3 E2 IsoGSM
4. S0 E2 ECHAMwiso
5. S0 E1 ECHAMwiso
6. S3 E2 ECHAMwiso

The different parameterisations of land and ocean evaporation only affect the isotopes. The S0 E2 simulations serve as the reference simulations, while S0 E1 and S3 E2 are the experiments for ocean and land evaporation respectively.

**5.2.2 Linear correlations**

The Pearson correlation coefficient $r$ (Pearson, 1895) is a measure for the linear dependence of two variables $x$ and $y$, and is defined as:

$$
 r = \frac{\sum_{n=1}^{N} (x^n - \bar{x})(y^n - \bar{y})}{\sqrt{\sum_{n=1}^{N} (x^n - \bar{x})^2 \sum_{n=1}^{N} (y^n - \bar{y})^2}}
$$

(5.1)

where $x^n$ and $y^n$ denote single values of the two variables, and $\bar{x}$ and $\bar{y}$ denote their mean. Hence, $r$ can be used to determine if and how the temporal variations of the isotope values are (linearly) dependent on meteorological variables. Here we focus on the correlation of temperature $T$ and precipitation amount $P$ with $\delta^2\text{H}$, and surface temperature $T_s$ and relative humidity at the lowest model level $h_s$ (calculated with respect to saturation at the surface temperature) with deuterium excess, since these meteorological variables are presumably the main drivers of the two isotope parameters. The maximum of $h_s$ is set to 200\% to avoid unrealistically high values over cold
land surfaces. The correlations are calculated for every model grid point at the lowest model level, and on three different time scales:

1. Daily correlations are calculated from the 240 hourly instantaneous values of each calendar day (e.g., 1 January 2002 – 1 January 2011), and averaged over the year. They show the average daily cycle.

2. Monthly correlations are calculated from the 280 to 310 daily means of each month (e.g., January 2002 – January 2011), also averaged over the year. They show the average monthly cycle.

3. Yearly correlations are calculated from the 120 monthly means of the ten years (2002 – 2011). They show the average annual cycle.

The correlations of the isotope values with local meteorological variables will provide an answer to question 1 (Section 5.1) from an Eulerian perspective.

5.2.3 Trajectories

Isotope values strongly depend on the meteorological history of air parcels. For example, \( \delta^2 \)H reflects the rainout history of air parcels rather than the accumulated precipitation at a given location, and the deuterium excess is generally used as a measure for the conditions at the moisture sources. Therefore, the meteorological variables are also traced along backward trajectories, using the Lagrangian Analysis Tool (Lagranto; Sprenger and Wernli, 2015).

The trajectories are started every 6 hours from the first, third, and fifth lowest model level of every second grid point (corresponding to approximately 10 m, 69 m and 179 m above the surface). They are calculated with 1 hourly input fields and go seven days back in time or until they leave the model domain. Along the trajectories, one out of eight process categories (land evaporation, ocean evaporation, mixing in, liquid cloud formation, ice cloud formation, mixed phase cloud formation, mixing out, no process) is assigned to every time step, based on the change in specific humidity, the location, temperature and relative humidity of the trajectory. The case distinction for the process allocation is shown schematically in Figure 5.3 and is described in the following.

**Process allocation**

The process allocation follows the approach of Meyer (2016). If specific humidity increases during a certain time step \( (\Delta q > \Delta q_{\text{min}}) \), moisture is assumed to have evaporated from the surface or to be mixed into the air parcel (i.e., the parcel mixes with moister air). The distinction between evaporation and mixing is made based on the trajectory’s height \( z \) compared to the boundary layer height \( BLH \) and the sign of the
evaporation flux $E$ from the surface. If the trajectory is located within an extended boundary layer, hence if $1.5 \cdot BLH \geq z$ (where the factor 1.5 takes into account the uncertainty of the boundary layer height parameterisation in COSMO), and the evaporation flux is positive, hence $E > 0$, the moisture increase is assigned to evaporation, if not it is assigned to mixing. Evaporation is said to originate from the ocean if the land sea mask $LSM$ at the trajectory’s location is $\leq 0.75$, and from land otherwise.

If specific humidity decreases ($\Delta q < -\Delta q_{\text{min}}$), moisture is assumed to have condensed or to be mixed out of the air parcel (i.e., it mixes with drier air). The distinction between condensation and mixing is made based on the relative humidity $h$ with respect to liquid water in the air parcel. If $h \geq 80\%$, the probability for subgrid-scale condensation is high, and the moisture decrease is assigned to condensation, if not it is assigned to mixing. The condensate is liquid if $T > 0^\circ C$, solid (ice) if $T < -23^\circ C$, and mixed phase if $-23^\circ C \leq T \leq 0^\circ C$.

To avoid noise, a minimum change of specific humidity $\Delta q_{\text{min}} = 0.01$ g/kg is required. If $-\Delta q_{\text{min}} \leq \Delta q \leq \Delta q_{\text{min}}$, no process is assigned to the time step.

**Weighting of processes with moisture content**

An air parcel typically experiences several moisture uptakes and losses. Processes occurring earlier during the transport of the air parcel therefore contribute less to its final composition, since part of the signal is lost during moisture losses and overwritten by later moisture uptakes. The relative contribution of a signal at time $n$ is proportional
to the amount of final moisture $q_{\text{fin}}^n$ at time $n$ that is still contained in the air parcel at its arrival point (at time $N$). To determine $q_{\text{fin}}^n$ the corresponding fraction of moisture $f_{\text{fin}}^n = q_{\text{fin}}^n / q^n$ is calculated. With $f_{\text{fin}}^N = 1$ by definition, $f_{\text{fin}}^n$ along the trajectories can be derived backward in time:

$$f_{\text{fin}}^n = f_{\text{fin}}^{n+1} \cdot \min(q^{n+1}/q^n, 1) \quad (5.2)$$

$$q_{\text{fin}}^n = f_{\text{fin}}^n \cdot q^n \quad (5.3)$$

where $\min(q^{n+1}/q^n, 1)$ denotes the minimum of 1 and the ratio of specific humidities at time $n + 1$ and $n$. This weighting is equivalent to the weighting applied in the moisture source diagnostic by Sodemann et al. (2008b). Figure 5.4 shows the time series of $q$, $q_{\text{fin}}$, and $f_{\text{fin}}$ along an example trajectory. If $q$ decreases from time $n$ to time $n + 1$ (forward), $q_{\text{fin}}$ stays constant, while $f_{\text{fin}}$ increases. This means that the contributions of the times $n$ and $n + 1$ to the air parcel’s final composition are equal, since part of the moisture at time $n$ is lost at time $n + 1$. If $q$ increases, $q_{\text{fin}}$ increases proportionally, while $f_{\text{fin}}$ stays constant. This means that the contribution of time $n + 1$ is larger than the contribution of time $n$, since the air parcel takes up new moisture, which partly overwrites the signal from time $n$. If $q$ stays constant, both $q_{\text{fin}}$ and $f_{\text{fin}}$ stay constant as well.

**Meteorological variables**

The trajectories provide Lagrangian information about temperature, precipitation amount, surface temperature and relative humidity ($T_L$, $P_L$, $T_s,L$ and $h_s,L$) experienced...
by the air parcels. \( T_L \) is here defined as the mean temperature along the trajectories weighted with \( q_{fin} \), and corresponds to the temperature that controlled the saturation vapour pressure and consequently the rainout of the air parcels. \( P_L \) is the rainout of the trajectories, which we define as the ratio between their relative moisture losses due to cloud formation (where \( h \geq 80\% \)) and moisture uptakes (following Gigandet, 2010). Hence:

\[
T_L = \frac{\sum_{n=0}^{N} q_{fin}^n \cdot T^n}{\sum_{n=0}^{N} q_{fin}^n} \quad (5.4)
\]

\[
P_L = \frac{\sum_{n_c=0}^{N_c-1} \Delta q_{nc} / q_{nc}^c}{\sum_{n_u=0}^{N_u-1} \Delta q_{nu} / q_{nu}^u} \quad \text{with} \quad \Delta q^n = |q^{n+1} - q^n| \quad (5.5)
\]

The subscripts \( c \) and \( u \) denote time steps with cloud formation events and moisture uptakes (due to evaporation and mixing), respectively. \( T_{S,L} \) and \( h_{S,L} \) are considered only in evaporation regions, where \( E > 0 \) and \( 1.5 \cdot BLH \geq z \). They are weighted with the relative contribution of the moisture uptakes, which can be calculated from the changes in \( q_{fin} \) during each time step:

\[
T_{S,L} = \frac{\sum_{n_e=0}^{N_e-1} \Delta q_{fin}^{ne} \cdot T_s^{ne}}{\sum_{n_e=0}^{N_e-1} \Delta q_{fin}^{ne}} \quad (5.6)
\]

\[
h_{S,L} = \frac{\sum_{n_e=0}^{N_e-1} \Delta q_{fin}^{ne} \cdot h_s^{ne}}{\sum_{n_e=0}^{N_e-1} \Delta q_{fin}^{ne}} \quad (5.7)
\]

where the subscript \( e \) denotes time steps with moisture uptakes due to evaporation. \( h_s \) is again calculated with respect to saturation at the surface temperature.

The same correlations as for the Eulerian versions of \( T, P, T_s \) and \( h_s \) (see above) are then calculated for the Lagrangian versions. This will provide an answer to question 1 (Section 5.1) from a Lagrangian perspective. Of particular interest are also the differences between the two approaches.
Impact of processes

Apart from defining moisture source locations and rainout, the processes specified in Section 5.2.3 can also directly be linked to the changes in δ²H and deuterium excess (Δδ²H and Δd) along the trajectories. Considering only the moisture still contained in the air parcel at its arrival point (qⁿ₉), the air parcel's final isotope ratio δᴺ can be reformulated to express the sum of the initial isotope ratio δ₀ and the changes during transport, all weighted with qⁿ₉:

\[ q^{N} \cdot \delta^{N} = q^{0} \cdot \delta^{0} + (q^{1} \cdot \delta^{1} - q^{0} \cdot \delta^{0}) + \cdots + (q^{N} \cdot \delta^{N} - q^{N-1} \cdot \delta^{N-1}) \]

\[ = q^{0} \cdot \delta^{0} + \sum_{n=0}^{N-1} (q^{n+1} \cdot \delta^{n+1} - q^{n} \cdot \delta^{n}) \]

\[ = q^{0} \cdot \delta^{0} + \sum_{n=0}^{N-1} \Delta(q^{n} \cdot \delta^{n}) \]  \hspace{1cm} (5.8)

Hence, the contribution of a process k to the final isotopic composition is:

\[ \Delta \delta_{k} = \sum_{n_{k}=0}^{N_{k}-1} \Delta(q^{n_{k}} \cdot \delta^{n_{k}}) / q^{N} \]  \hspace{1cm} (5.9)

where the subscript k denotes time steps assigned to process k. Comparison of the different δ²Hₓ and δₓ will then show which processes are responsible for changes of the isotopic composition of the air parcels during their transport (part 1 of question 2, Section 5.1). The influence of the processes on isotopic variability (part 2 of question 2, Section 5.1) is addressed by considering days and months when δ²H or deuterium excess are unusually high or low with respect to the ten-year monthly climatology from the model simulation. The difference of Δδ²Hₓ and Δδₓ between high and low anomaly days and months represents the contribution of the processes to the anomalies (and thus, to isotopic variability on the given time scale). For each grid point, the 912 days and 30 months with the highest and lowest δ²H and deuterium excess anomalies are selected, corresponding to the 75% and 25% percentiles (quartiles). The two samples are then averaged and subtracted.

5.2.4 Extratropical cyclones and fronts

For quantifying the impact of extratropical cyclones and fronts on the isotopes, we apply objective cyclone and front detection algorithms to the model output fields. Fronts...
are identified based on the gradient of equivalent potential temperature $\Theta_e$ at 950 hPa, 850 hPa and 700 hPa, using the technique of Jenkner et al. (2010). Cyclones are identified at the surface, as areas within closed contours of sea level pressure ($SLP$) around $SLP$ minima, following the technique of Wernli and Schwierz (2006) and Han-ley and Caballero (2012). 30% of the $SLP$ contours of a cyclone are allowed to cross the boundaries. Cyclones and fronts are analysed separately, but warm and cold fronts are not treated separately, since the distinction over orography is often difficult.

As a next step, air masses associated with a cyclone or front are identified. For this we apply two different approaches. The first (Eulerian) approach defines grid points inside a cyclone or front area as associated with a cyclone and front, respectively. Cyclone areas are defined as the area within the identified cyclone contours, and front areas are defined as the areas with an average distance of less than 300 km to the identified frontal lines. No distance limit is applied in the vertical. The second (Lagrangian) approach defines grid points whose backward trajectories have passed a cyclone or front area as associated with a cyclone and front, respectively. Thus, the second approach includes the grid points from the first approach, but extends the definition to air masses that used to belong to a cyclone or front, that either decayed or travelled in a different direction.

Finally we compare the isotope signals of air masses associated with a cyclone or front to air masses not associated with a cyclone or front for both approaches by calculating composites of the two air mass types and subtracting them. This will provide an answer to question 3 (Section 5.1).

5.3 Results

5.3.1 Model evaluation

Annual mean $\delta^2H$

Figure 5.5 shows $\delta^2H$ in precipitation (mean over 2002–2011) in the six COSMOiso simulations and in IsoGSM and ECHAMwiso, together with the GNIP measurements (IAEA/WMO, 2016). Only stations that measured during at least two of the ten years are considered. The values from COSMOiso and ECHAMwiso are accumulated, while the values from IsoGSM are instantaneous every 6 hours, and therefore not totally equivalent to the GNIP measurements. The isotope values are always weighted with precipitation amount, meaning that months with more precipitation contribute more to the mean value.

All COSMOiso simulations nicely reproduce the gradients from the continent to the ocean (continental effect) and from north to south (latitude effect), which are also
Figure 5.5: $\delta^{2}H$ in precipitation from (a–f) the six COSMOiso simulations, (g) IsoGSM and (h) ECHAMwiso. The GNIP measurements are shown as dots.
observed at the GNIP stations. The gradients are weaker in the simulations forced with IsoGSM (Figure 5.5 a,c,e) than in the simulations forced with ECHAMwiso (Figure 5.5 b,d,f), due to more enriched precipitation in the north of the domain, especially over land. This difference can also be seen in the GCM simulations (Figure 5.5 g,h) and follows from the more enriched water vapour in IsoGSM compared to ECHAMwiso over northeastern Europe.

The finer resolution of the COSMOiso simulations, and consequently their better representation of topography, reveals small-scale structures of $\delta^2$H that are not visible in the two GCMs. For example, the Atlas, Pyrenees, Carpathians or Balkan mountains clearly receive more depleted precipitation than their surrounding flatlands. Generally, the COSMOiso simulations tend to produce more depleted precipitation than the GCM they are forced with, which is mostly beneficial for the simulations using IsoGSM, but sometimes leads to underestimated $\delta^2$H in the simulations using ECHAMwiso (e.g., over the Atlantic or in Turkey).

The different parameterisations of land evaporation ($S_0$ / $S_3$) and ocean evaporation ($E_1$ / $E_2$) only have a minor influence on $\delta^2$H in the COSMOiso simulations.

**Time series of $\delta^2$H**

For evaluating interannual isotopic variability in the models, we consider time series of $\delta^2$H in monthly precipitation at three selected GNIP stations with different climates: Valentia (Ireland), Grimsel (Switzerland), and Athens-Penteli (Greece) (see Figure 5.1). The modelled $\delta^2$H values are linearly interpolated to these stations.

The Valentia observatory (Figure 5.6 a) lies at the southwestern tip of Ireland, east of Valentia Island, where it was situated originally and from which it still bears the name. The GNIP station is located just 9 m above sea level. During the years 2002 – 2011 it received on average 1635 mm of precipitation per year and the temperature varied around a mean of 11.13°C. Due to its oceanic climate the measured $\delta^2$H values are high, ranging from $-96^\circ/\circ$ to $4^\circ/\circ$ with a mean of $-32^\circ/\circ$, and vary largely on the monthly time scale. The models show difficulties in reproducing these short-term variations accurately, but the overall mean and variability of the simulated values agree well with the measurements, except for a slight underestimation of $\delta^2$H by the COSMOiso simulations forced with ECHAMwiso.

The Grimsel station (Figure 5.6 b) is located at the Grimsel pass in the Swiss Alps, at 1950 m above sea level. During the years 2002 – 2008 it received on average 1761 mm of precipitation per year, while the mean temperature was 2.35°C. The measured $\delta^2$H values are lower than at Valentia and show a strong and rather regular annual cycle in correlation with temperature, between $-159^\circ/\circ$ in winter and $-27^\circ/\circ$ in summer with a mean of $-95^\circ/\circ$. Due to the complex topography in this area the spread within the four
Figure 5.6: Measured and modelled monthly mean $\delta^2\text{H}$ in precipitation, temperature and precipitation amount at the GNIP stations (a) Valentia, (b) Grimsel and (c) Athens-Penteli. The shaded area shows the range between the minimum and maximum value of the four surrounding gridpoints.
surrounding grid points in the models is large. Nevertheless the COSMOiso simulations and ECHAMwiso reproduce the mean and variability of δ²H very well. IsoGSM, with its quite coarse resolution, overestimates δ²H during the whole period.

The station at Athens-Penteli (Figure 5.6 c) is one of two GNIP stations situated in the capital of Greece. It lies close to the southwestern slope of Mount Pentelikon, at 498 m above sea level. The average annual precipitation at the site during the years 2002–2011 was 566 mm and the mean temperature was 15.25°C. Here the measured δ²H values are again rather high, ranging from –83‰ to 5‰ with a mean of –36‰. The lowest δ²H values are often concurrent with maxima in precipitation, and are nicely reproduced by the models, although precipitation in the same months is often underestimated. The mean and variability in the models also agree well with the measurements, except for a slight overestimation of δ²H in ECHAMwiso, which is possibly connected to its slight overestimation of temperature (not shown).

Seasonal mean and variability of δ²H

Figure 5.7 shows the modelled against measured seasonal mean δ²H in precipitation. The modelled δ²H values are again linearly interpolated to the GNIP stations. At all stations only the months are considered, for which a GNIP measurement and a value from all models is available. Furthermore, only stations are shown with measurements in at least half of the months in the respective season.

According to this analysis, summer is the most difficult season to simulate, with all models having a too flat slope between the lowest and the highest δ²H. In the other seasons the distribution of the values is better, and the regression lines are often quite close to the 1:1 line. The COSMOiso simulations forced with ECHAMwiso are closest to the measurements with only a small negative bias in spring, autumn and winter. The simulations forced with IsoGSM overestimate the lowest values, and consequently have a too flat slope. ECHAMwiso performs better than IsoGSM and the IsoGSM forced COSMOiso simulations.

Also the statistical distributions of the monthly δ²H values (Figure 5.8) are best reproduced by the COSMOiso simulations forced with ECHAMwiso. They have more depleted and wider distributions than IsoGSM, ECHAMwiso and the COSMOiso simulations forced with IsoGSM, and nicely match the distribution in the GNIP measurements in all seasons except winter. The IsoGSM forced COSMOiso simulations, as well as IsoGSM and ECHAMwiso, generally overestimate the median δ²H and underestimate its variability. Note that the statistical distributions in summer are nicely reproduced by the models, especially the COSMOiso simulations forced with ECHAMwiso, in contrast to the separate values at each station (cf. Figure 5.7). This indicates that in summer
local processes are more important than in the other seasons, and small displacements of processes in the models can lead to large deviations of the simulated values, which even out in the statistical distribution.

Figure 5.9 gives a summary of validation measures for the models: mean absolute error (MAE), mean bias error (MBE), and variance error (VE). They are calculated from the measured and modelled 10-year seasonal mean $\delta^2$H values ($o^n$ and $x^n$) as follows:

$$
MAE = \frac{1}{N} \sum_{n=1}^{N} |x^n - o^n|, \quad MBE = \frac{1}{N} \sum_{n=1}^{N} (x^n - o^n), \quad VE = \left( \frac{1}{N} \sum_{n=1}^{N} \frac{x^n - 1}{N} \sum_{n=1}^{N} o^n \right) \left( \frac{1}{N} \sum_{n=1}^{N} o^n - 1 \right) \left( \frac{1}{N} \sum_{n=1}^{N} x^n \right)^2
$$

(5.10)

where $n$ represents the value at one specific GNIP station and $N$ is the total number of stations in the model domain, which measured at least half of the months in the

![Graphs showing seasonal mean values of $\delta^2$H in precipitation from the models with respect to the GNIP measurements.](image)

**Figure 5.7:** Seasonal mean values of $\delta^2$H in precipitation from the models with respect to the GNIP measurements. Each dot represents one GNIP station, averaged over the season and over ten years. The lines are orthogonal regression lines (Adcock, 1878).
respective season. Qualitatively, MAE, MBE and VE can also be seen in Figures 5.7 and 5.8.

In terms of MAE (Figure 5.9a) the COSMOiso simulations forced with ECHAMwiso clearly outperform the other simulations and models in spring, summer and autumn, while in winter the MAEs are almost equal. The MBE (Figure 5.9b) is negative for the COSMOiso simulations forced with ECHAMwiso, and positive for IsoGSM, ECHAMwiso and the COSMOiso simulations forced with IsoGSM, mainly due to the overestimation of the depleted values, as discussed above. Notably IsoGSM alone has a lower MAE and MBE in summer than the corresponding COSMOiso simulations and only a slightly higher MAE and MBE in the other seasons. This could be related to the nudging that was applied in IsoGSM but not in COSMOiso. The VE (Figure 5.9c) again shows the almost perfect variability of the $\delta^2$H values in the COSMOiso simulations forced with ECHAMwiso. The other simulations and models all have a negative VE, i.e., a too narrow distribution of $\delta^2$H.

Figure 5.8: Probability density functions of monthly mean $\delta^2$H from the models and the GNIP measurements.
Hence, the COSMOiso simulations using initial and boundary data from ECHAMwiso produce the best results for $\delta^2$H in all these aspects. Between the simulations the differences are rather small. The application of TERRAiso (S3) instead of external data (S0) increases the MAE, MBE, and VE slightly, while the two parameterisations for ocean evaporation (E1 and E2) are very similar. However, the latter can be expected to have a larger impact on deuterium excess, since it affects the nonequilibrium fractionation factor during evaporation. This will be examined in the following.

### Annual mean deuterium excess

Figure 5.10 shows the mean deuterium excess in precipitation in the six COSMOiso simulations and in IsoGSM and ECHAMwiso, together with the GNIP measurements. Again only stations which measured during at least two years are considered. Compared to the annual means of $\delta^2$H there are three main differences. First, deuterium excess varies on small horizontal scales and differs more between the models and the measurements. This indicates that nonequilibrium fractionation, which to first order governs the deuterium excess, is more difficult to simulate than equilibrium fractionation, which to first order governs $\delta^2$H and $\delta^{18}$O. Second, the parame-

![Graph showing mean absolute error (MAE), mean bias error (MBE), and variance error (VE) of seasonal mean $\delta^2$H in precipitation from the models with respect to the GNIP measurements.](image-url)
rerisation of ocean evaporation, while not affecting $\delta^2$H, has a large impact on the deuterium excess, because it changes the nonequilibrium fractionation factor. The wind speed independent formulation (E2) produces higher deuterium excess than the classical formulation (E1) in the whole domain, but especially over the Mediterranean (Figure 5.10 c,d,e,f compared to Figure 5.10 a,b), due to its overall stronger nonequilibrium fractionation (smaller $\alpha_k$; see Figure 5.2). Third, the selection of the initial and boundary data, while being the dominant factor for $\delta^2$H, only has a minor influence on the deuterium excess (Figure 5.10 a,c,e compared to Figure 5.10 b,d,f). The COSMOiso simulations forced with IsoGSM produce slightly higher values than the COSMOiso simulations forced with ECHAMwiso. This difference is also reflected in the precipitation from the two GCMs alone with ECHAMwiso producing lower deuterium excess in precipitation than IsoGSM, especially over the Mediterranean (Figure 5.10 g,h). Furthermore, the application of TERRAiso (S3) instead of external data (S0) leads to slightly lower deuterium excess over northeastern Europe, but the differences are rather small.

**Time series of deuterium excess**

Time series of deuterium excess in monthly precipitation are extracted for the same three GNIP stations as for $\delta^2$H. At the Valentia observatory the deuterium excess, in contrast to $\delta^2$H, shows a weak annual cycle around a mean of 9 $^\circ$/oo, which is negatively correlated with temperature (high $d$ in winter, low $d$ in summer). This can also be seen in the COSMOiso simulations, and, to a smaller extent, in ECHAMwiso and IsoGSM. It is the typical annual cycle of deuterium excess in the Northern Hemisphere, caused by stronger evaporation from the ocean in winter than in summer (Pfahl and Sodemann, 2014).

At Grimsel there is no annual cycle of deuterium excess. The mean is similar as at Valentia (12 $^\circ$/oo), but the variability is much smaller, with a majority of the monthly values between 11 $^\circ$/oo and 14 $^\circ$/oo. The models generally underestimate the deuterium excess at Grimsel, most of all the COSMOiso simulation forced by ECHAMwiso and using the classical parameterisation of $\alpha_k$ (S0 E1 ECHAMwiso).

In Athens the deuterium excess has a high variability, reaching values up to 21 $^\circ$/oo in winter and down to −17 $^\circ$/oo in late spring or early summer. The negative values often occur in months with very little precipitation. This could be connected to evaporation of falling rain, which enhances the deuterium excess in vapour, and lowers the deuterium excess in rain. The minima are only reproduced by the COSMOiso simulations, where below cloud interactions of rain and vapour are modelled explicitly (in contrast to IsoGSM and ECHAMwiso, which use prescribed equilibration rates according to the type of precipitation and relative humidity). The COSMOiso simulations tend to over-
Figure 5.10: Deuterium excess in precipitation from (a–f) the six COSMOiso simulations, (g) IsoGSM and (h) ECHAMwiso. The GNIP measurements are shown as dots.
Figure 5.11: Measured and modelled monthly mean deuterium excess in precipitation, temperature and precipitation amount at the GNIP stations (a) Valentia, (b) Grimsel and (c) Athens-Penteli. The shaded area shows the range between the minimum and maximum value of the four surrounding gridpoints.
estimate both the number and the magnitude of these minima, maybe since they in general also underestimate the amount of precipitation. The higher deuterium excess in winter is likely connected to strong evaporation over the Mediterranean due to the advection of cold and dry air. These values are well reproduced by the E2 COSMOiso simulations (using the wind speed independent value for $\alpha_k$), and slightly underestimated by the E1 COSMOiso simulations (using the classical formulation of $\alpha_k$), as well as by IsoGSM and ECHAMwiso.

**Seasonal mean and variability of deuterium excess**

Figure 5.12 shows the modelled against measured mean deuterium excess in precipitation divided by season, again for all stations which measured at least half of the months in the respective season, and including only months with a GNIP measurement and a value from all models.

![Graphs showing seasonal mean values of deuterium excess](image)

**Figure 5.12:** Seasonal mean values of deuterium excess in precipitation from the models with respect to the GNIP measurements. Each dot represents one GNIP station, averaged over the season and over ten years. The lines are orthogonal regression lines (Adcock, 1878).
Clearly the deuterium excess values are more scattered than the $\delta^2$H values (cf. Figure 5.7), underlining that nonequilibrium fractionation is more difficult to represent in the models than equilibrium fractionation. The regression lines are mostly either too flat or too steep. Except for autumn (and summer for the COSMOiso simulations forced with ECHAMwiso), the values from the E2 COSMOiso simulations are closer to the 1:1 line than the values from IsoGSM, ECHAMwiso and the E1 COSMOiso simulations. The probability density functions of the same monthly deuterium excess values are also less well reproduced by the models (Figure 5.13) compared to the corresponding functions of $\delta^2$H (cf. Figure 5.8). The distributions are mostly too narrow, especially in IsoGSM and ECHAMwiso. Only the E2 COSMOiso simulations forced with IsoGSM match well with the measurements. As already apparent from Figure 5.10, using E1 instead of E2 or ECHAMwiso instead of IsoGSM input data leads to lower deuterium excess values in all seasons (and mostly also to a narrower distribution).

Figure 5.14 shows the MAE, MBE and VE of the models for deuterium excess, calculated following Equation 5.10. Here the ECHAMwiso forced COSMOiso simulations

![Figure 5.13: Probability density functions of monthly mean deuterium excess from the models and the GNIP measurements.](image-url)
are similar to the IsoGSM forced COSMOiso simulations. However, a clear difference in terms of performance is visible between the two parameterisations of ocean evaporation. E1 COSMOiso simulations have a larger MAE and more negative MBE than the corresponding E2 COSMOiso simulations. Within the E2 COSMOiso simulations the results are similar, except for the high MAE and MBE of the S3 E2 ECHAMwiso simulation in summer. IsoGSM and ECHAMwiso outperform the E1 COSMOiso simulations in terms of MAE and MBE, but have a much larger VE due to their too narrow distribution of deuterium excess values (cf. Figure 5.13).

In summary, according to this evaluation, the COSMOiso simulation using ECHAMwiso as initial and boundary data, soil isotope content from external data, and the wind speed independent formulation of the nonequilibrium fractionation factor (S0 E2 ECHAMwiso) produces the best results for $\delta^2$H and deuterium excess when compared to GNIP measurements. We therefore use this simulation for the analysis in the following sections.

![Graph showing MAE, MBE, and VE for seasonal mean deuterium excess](image_url)

**Figure 5.14:** Mean absolute error (MAE), mean bias error (MBE), and variance error (VE) of seasonal mean deuterium excess in precipitation from the models with respect to the GNIP measurements.
5.3.2 Correlations

Eulerian and Lagrangian variables

Figure 5.15 shows the daily, monthly and yearly correlations\(^1\) of the Eulerian and Lagrangian versions of the selected meteorological variables (temperature, precipitation amount, relative humidity and surface temperature). The stippling indicates where

(a) \(T\) and \(T_L\)

(b) \(P\) and \(P_L\)

(c) \(h_s\) and \(h_{s,L}\)

(d) \(T_s\) and \(T_{s,L}\)

\(^1\)Daily correlations show the mean correlations of the hourly values for each calendar day, monthly correlations show the mean correlations of the daily values for each month, and yearly correlations show the correlations of the monthly values (see Section 5.2.2).

**Figure 5.15**: Daily, monthly and yearly correlations of (a) \(T\) and \(T_L\), (b) \(P\) and \(P_L\), (c) \(h_s\) and \(h_{s,L}\), and (d) \(T_s\) and \(T_{s,L}\). Stippling indicates areas where \(p < 0.01\).
the correlations are significant, i.e., where the probability for getting the correlation by chance is $p < 1\%$.

The local temperature $T$ and the weighted mean temperature along the trajectories $T_L$ are positively correlated everywhere and on all time scales, with increasing values on longer time scales (Figure 5.15 a). The strong positive correlation on long time scales can be explained by the seasonal cycle, which is the main driver of monthly mean temperature. On short time scales, local effects, e.g., clouds or adiabatic cooling / warming, can lead to deviations between $T$ and $T_L$ and consequently weaker correlations.

The local precipitation amount $P$ and the rainout along the trajectories $P_L$ are mostly unrelated on all time scales (Figure 5.15 b). Only on the yearly time scale a positive correlation can be found over the Mediterranean. This highlights the very different character of the two definitions of precipitation amount.

The local relative humidity $h_s$ and the relative humidity at the moisture sources $h_{s,L}$ are again mostly positively correlated (Figure 5.15 c). Exceptions are the land surface on the daily time scale, where the correlations are weak, and the northwestern part of Europe and eastern part of North Africa on the yearly time scale, where the correlations are even negative. Weak and negative correlations indicate nonlocal moisture sources.

The local surface temperature $T_s$ and the surface temperature at the moisture sources $T_{s,L}$ are weakly positively correlated on the daily time scale and more strongly positively correlated on the monthly and yearly time scale (Figure 5.15 d). Thereby an interesting land-sea contrast, opposite to the contrast of $h_s$ and $h_{s,L}$, can be observed on the daily and monthly time scale.

**Isotopes**

The correlations of the three isotope parameters $\delta^2H$, $\delta^{18}O$ and deuterium excess are shown in Figure 5.16. The two first-order parameters ($\delta^2H$ and $\delta^{18}O$) are highly positively correlated on all three time scales (Figure 5.16 a). This indicates that equilibrium effects are the dominant factor for their variability. Moreover it means that all correlations shown in the following for $\delta^2H$ are also valid for $\delta^{18}O$. The deuterium excess, on the other hand, is mostly negatively correlated with $\delta^2H$, especially over the ocean, and on the yearly time scale also over land (Figure 5.16 b). The negative correlation is partly an artefact of the deuterium excess definition (see Chapter 3), however in this case most likely due to the negative correlation of temperature and relative humidity, which are positively correlated with $\delta^2H$ and deuterium excess, respectively (see below).
Chapter 5. Seasonal Isotopic Variability

(a) \( \delta^2H \) and \( \delta^{18}O \)

(b) \( \delta^2H \) and deuterium excess

Figure 5.16: Daily, monthly and yearly correlations of (a) \( \delta^2H \) and \( \delta^{18}O \), and (b) \( \delta^2H \) and deuterium excess in water vapour. Stippling indicates areas where \( p < 0.01 \).

Temperature and \( \delta^2H \)

Temperature and \( \delta^2H \) are almost everywhere positively correlated, with the highest values (up to 0.95) on the yearly time scale (Figure 5.17). This confirms the temperature effect found by Dansgaard (1964). Exceptions are the southwestern tip of the Iberian peninsula, and North Africa on the daily and monthly time scale, where there

(a) Eulerian

(b) Lagrangian

Figure 5.17: Daily, monthly and yearly correlations of temperature and \( \delta^2H \) in water vapour from (a) the Eulerian and (b) the Lagrangian perspective. Stippling indicates areas where \( p < 0.01 \).
is nearly no correlation. Both the Eulerian and Lagrangian versions of temperature ($T$ and $T_L$) show similar results, which is in accordance with the high correlation between $T$ and $T_L$ in Figure 5.15 a.

**Precipitation amount / rainout and $\delta^2H$**

Precipitation amount and rainout do not correlate strongly with $\delta^2H$ on the daily and monthly time scale (Figure 5.18). Only on the yearly time scale large areas with significant negative correlations can be found. Thereby the Eulerian and Lagrangian versions lead to very different results. The Eulerian precipitation amount is negatively correlated with $\delta^2H$ over the ocean and mostly unrelated to $\delta^2H$ over land. The Lagrangian rainout, in contrast, is positively correlated with $\delta^2H$ over the Atlantic in the west of the domain, and negatively correlated over Europe, North Africa and the Mediterranean in the east of the domain. Most air parcels arriving in the west entered the domain only shortly before through the western boundary, meaning that a large

(a) Eulerian (precipitation)

(b) Eulerian (vapour)

(c) Lagrangian

**Figure 5.18:** Daily, monthly and yearly correlations of precipitation amount / rainout and $\delta^2H$ in water vapour from (b) the Eulerian and (c) the Lagrangian perspective. The Eulerian correlations are also shown for $\delta^2H$ in precipitation (a). Stippling indicates areas where $p < 0.01$. 
part of their rainout history is unknown. Therefore, the positive correlation should not be overinterpreted. The negative correlation in the east nicely shows the Rayleigh condensation effect (and Dansgaard’s amount effect), where rainout leaves the remaining vapour depleted in heavy isotopes. This effect is also visible for the Eulerian precipitation amount over the ocean. Interestingly, $\delta^{2}H$ in vapour and precipitation show very similar correlations with precipitation amount. This may be due to the imprint of the isotope signal in precipitation on vapour or vice versa.

**Relative humidity and deuterium excess**

Relative humidity with respect to the sea surface temperature is strongly negatively correlated with deuterium excess over the ocean (Figure 5.19), as predicted by the Craig-Gordon equation (Equation 2.11). This is also partly valid over land, if only the moisture sources are considered (i.e., $h_{S,L}$; Figure 5.19 b). For the Eulerian version of $h_{S}$ over land there is no correlation on the daily and monthly time scale, and a quite strong positive correlation on the yearly time scale, except over the Alps and in northeastern Europe (Figure 5.19 a). The positive correlation reflects the similar seasonal cycles of relative humidity and deuterium excess over land, with both generally having higher values in winter than in summer. However, a causality is unlikely, since there is mostly no correlation between relative humidity at the moisture sources ($h_{S,L}$) and deuterium excess.

![Figure 5.19](image-url)

**Figure 5.19:** Daily, monthly and yearly correlations of relative humidity and deuterium excess in water vapour from (a) the Eulerian and (b) the Lagrangian perspective. Stippling indicates areas where $p < 0.01$. 
Surface temperature and deuterium excess

Surface temperature is mostly negatively correlated with deuterium excess (Figure 5.20). The strongest correlations can be found over the ocean on the daily and monthly time scale, if only the moisture sources are considered (i.e., $T_s, L$; Figure 5.20 b) and over land on the yearly time scale for both versions of $T_s$. This result is exactly opposite to what would be predicted by the Craig-Gordon equation, and what many studies have used previously. It can only be explained by assuming that sea surface temperature is not the main driver of deuterium excess variability.

Overview

Table 5.1 gives an overview over the correlations of the Eulerian variables and the isotopes. Apart from $T$ and $T_s$ over land, the strongest correlation can be found for $d$ and $h_s$ over the ocean, with values below $-0.8$ on all three time scales. This correlation is even stronger than the correlation of $\delta^2 H$ and $T$, which only reaches 0.8 over land on the yearly time scale. Other quite strong correlations can be found for $\delta^2 H$ and $h_s$, and for $d$ and $T$ over the ocean. They are likely related to the positive correlation of $h_s$ and $T$ over the ocean, which is caused by the advection of different air masses (Pfahl and Niedermann, 2011): typically, air masses advected from higher latitudes originate from higher levels and are therefore drier than air masses advected from lower latitudes. $d$ and $T_s$ are mostly unrelated, especially over the ocean, as already seen in Figure 5.20. This is also reflected in the generally low correlations between $T_s$ and $h_s$. Furthermore,

(a) Eulerian

(b) Lagrangian

Figure 5.20: Daily, monthly and yearly correlations of surface temperature and deuterium excess in water vapour from (a) the Eulerian and (b) the Lagrangian perspective. Stippling indicates areas where $p < 0.01$. 
### Table 5.1: Mean correlations of $\delta^2$H, $d$, $T$, $P$, $h_s$, and $T_s$ (Eulerian versions) over ocean (left entries) and over land (right entries). The top, middle, and bottom entries represent the daily, monthly and yearly correlations, respectively. The colours correspond to the colours in Figures 5.15–5.20.

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<tr>
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<th>$d$</th>
<th>$T$</th>
<th>$P$</th>
<th>$h_s$</th>
<th>$T_s$</th>
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<td>0.53 0.29</td>
<td>-0.18 0.09</td>
<td>0.56 0.12</td>
<td>0.10 0.21</td>
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<td>0.61 0.42</td>
<td>-0.22 0.06</td>
<td>0.62 0.12</td>
<td>0.14 0.37</td>
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<tr>
<td></td>
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<td>-0.53 0.13</td>
<td>0.76 -0.45</td>
<td>0.61 0.77</td>
</tr>
<tr>
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<td>-0.05 0.03</td>
<td>-0.83 0.02</td>
<td>0.01 -0.12</td>
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<td>-0.25 -0.44</td>
</tr>
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<td>0.62 -0.63</td>
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<tr>
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<td>0.01 -0.12</td>
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<td>-0.23 -0.18</td>
<td>0.38 -0.76</td>
<td>1.00 1.00</td>
</tr>
</tbody>
</table>

Many correlations become stronger on longer time scales, implying that additional unaccounted factors influence isotopic variability on short terms, which tend to average out on long terms.

### 5.3.3 Processes

#### Climatology

Figure 5.21 shows the ten-year mean $\delta^2$H and deuterium excess in water vapour on the first, third and fifth lowest model level ($\delta^2$H$_{fin}$ and $d_{fin}$) together with the separate contributions of the initial values ($\delta^2$H$_{ini}$ and $d_{ini}$) and the total changes along the trajectories induced by the processes specified in Section 5.2.3 ($\Delta\delta^2$H and $\Delta d$). $\delta_{ini}$ and $\Delta\delta$ are defined as (see Equations 5.8 and 5.9):

$$\delta_{ini} = \frac{q_{fin}^0 \cdot \delta^0}{q_{fin}^N}$$

$$\Delta\delta = \sum_{n=0}^{N-1} \frac{\Delta(q_{fin}^n \cdot \delta^n)}{q_{fin}^N}$$
By definition, the weighted initial values and the changes along the trajectories fully explain $\delta^2 H$ and $d$ at the trajectories’ arrival points ($\delta_{ini}^0 + \Delta \delta = \delta_{fin}^0$; see Equation 5.8). The percentage of moisture explained by the two terms ($q_{exp}$) is shown in contours and corresponds to $q_{fin}^0/q_{fin}^N$ for the initial values (Figure 5.21 c,d) and to $1 - q_{fin}^0/q_{fin}^N$ for the changes along the trajectories (Figure 5.21 e,f).

The north-south gradient of $\delta^2 H_{fin}$ (the latitude effect) (Figure 5.21 a) is already visible in $\delta^2 H_{ini}$ (Figure 5.21 c). However this is mainly due to the higher values of $q_{fin}^0/q_{fin}^N$ in the north than in the south, while $\delta^2 H^0$ alone has no north-south gradient (not shown). The processes ($\Delta \delta^2 H$; Figure 5.21 e) add the land-sea contrast (continental effect) to $\delta^2 H_{fin}$ and the depletion in topographic regions (altitude effect). $d_{ini}$ (Figure 5.21 d) shows a similar pattern as $\delta^2 H_{ini}$, but of the opposite sign. This again corresponds quite well to the pattern of $q_{fin}^0/q_{fin}^N$. The high values of $d_{ini}$ (Figure 5.21 b) in the south

**Figure 5.21**: Ten-year average of $\delta^2 H$ (left) and deuterium excess (right) in water vapour on the first, third, and fifth lowest model level (top) and the weighted contributions of the initial values (middle) and changes along the trajectories (bottom). The numbers show the mean contribution of each term to the final value ($\delta^2 H_{fin}$ and $d_{fin}$). The contours show $q_{exp}$ in %.
of the domain, especially over the Mediterranean, originate from the changes along the trajectories (Figure 5.21 f). The mean contribution of $\Delta \delta^2H$ to $\delta^2H_{\text{fin}}$ and $\Delta d$ to $d_{\text{fin}}$ are 59% and 73%, respectively. These parts can be further separated into the relative contributions of the different processes. They are shown in Figure 5.22 for $\delta^2H$ and in Figure 5.23 for deuterium excess. Note that for $\delta^2H$ all contributions are negative, since $\delta^2H$ in the moisture uptakes is (almost) always negative, and moisture decreasing processes typically also decrease $\delta^2H$. For deuterium excess the contributions are mostly positive but can also be negative, since the deuterium excess in the moisture uptakes is typically positive, but some processes lead to a decrease.

For $\delta^2H$, evaporation from the ocean and mixing with moister air contribute most with 36% and 25% on average, respectively. Evaporation from land, formation of liquid clouds, and mixing with drier air contribute with 12% each. The formation of mixed phase and ice clouds, and the time steps for which no process was assigned are only of minor importance. For the trajectories arriving over the ocean, evaporation from the ocean is the dominant process. Over land, mixing with moister and with drier air, evaporation from land and the formation of liquid clouds are more important than evaporation from the ocean.

The pattern corresponds quite well to the amount of moisture explained by the processes ($q_{\text{exp}}^k$). $q_{\text{exp}}^k$ is defined differently for moisture increasing processes and moisture decreasing processes. For evaporation from land, evaporation from the ocean, mixing with moister air, and the time steps for which no process was assigned it represents the percentage of final moisture ($q_{\text{fin}}$) added by the processes, and is defined as:

$$q_{\text{exp}}^k = \frac{\sum_{n_k=0}^{N_k-1} n_k \Delta q_{\text{fin}}^n}{q_{\text{fin}}^N}$$

(5.13)

For the formation of liquid clouds, mixed phase clouds and ice clouds, and mixing with drier air $q_{\text{exp}}^k$ represents the average percentage of $q_{\text{fin}}$ that experienced the processes, and is defined as:

$$q_{\text{exp}}^k = \frac{1}{N} \cdot \frac{\sum_{n_k=0}^{N_k-1} n_k q_{\text{fin}}^n}{q_{\text{fin}}^N}$$

(5.14)

For deuterium excess, evaporation from the ocean is clearly the most important process with 65% contribution on average. The other two moisture increasing processes, mixing with moister air and evaporation from land, account for 21% and 15%, respectively. Cloud formation processes and mixing with drier air have almost no influence.
The formation of liquid clouds shows a small negative contribution (–3 %), meaning that it slightly decreases the deuterium excess. Again, evaporation from the ocean is most important for the trajectories arriving over the ocean, while for the trajectories arriving over land evaporation from land and mixing with moister air are dominant. The contribution of the moisture increasing processes to the final deuterium excess also corresponds well to their respective $q^k_{exp}$, whereas no relation to $q^k$ can be found for the moisture decreasing processes.

In winter the contribution of the processes to both $\delta^2$H and deuterium excess is larger than in summer (Figure 5.24). $\Delta \delta^{2}H/\delta^{2}H_{fin}$ varies between 67 % and 48 %, and $\Delta d/d_{fin}$

**Figure 5.22:** Contributions of the processes to $\Delta \delta^{2}H$ in Figure 5.21e. The numbers show the mean contribution of each process and the contours show the percentage of moisture explained by each process ($q^k_{exp}$; see Equations 5.13 and 5.14). Note the different colour scales for $q^k_{exp}$ between the left and right hand side.
varies between 80% and 64%. This variability is mainly due to the larger impact of evaporation from the ocean in winter than in summer. In contrast, evaporation from land has a larger impact in summer than in winter, but its contribution to $\delta^2H_{\text{fin}}$ and $d_{\text{fin}}$ is much smaller. The contribution of liquid clouds and the two mixing processes stays roughly constant throughout the year. Mixed phase clouds contribute only in the cold season, and ice clouds have almost no influence. Again visible is the slight negative contribution of liquid and mixed phase cloud formation processes to deuterium excess (Figure 5.24 b).

Figure 5.23: Contributions of the processes to $\Delta d$ in Figure 5.21f. The numbers show the mean contribution of each process and the contours show the percentage of moisture explained by each process ($q^k_{\text{exp}}$; see Equations 5.13 and 5.14). Note the different colour scales for $q^k_{\text{exp}}$ between the left and right hand side.
Figure 5.24: Time series of the ten-year daily mean (a) $\delta^2$H and (b) deuterium excess (white lines) in near-surface vapour, averaged over the domain, and the weighted contributions of the initial values and processes (colours).

Anomalies

Figure 5.25 shows the difference in the anomalies of $\delta^2$H with respect to the ten-year monthly mean between the 25% of days and months when they were highest and the 25% of days and months when they were lowest (25% roughly corresponds to 912 days and 30 months, respectively). The stippling again indicates where the probability of getting the difference between the two samples (high and low) by chance is $p < 1\%$. $p$ was calculated from a two-sided t-test for the null hypothesis that the samples have identical mean values. The difference in $\delta^2$H is larger over land than over ocean with values above 50‰ for the daily, and above 25‰ for the monthly anomalies (Figure 5.25 a). This means that the variability of $\delta^2$H is higher over land than over ocean. Apart from the scale being halved for the monthly compared to the daily anomalies, the two patterns look very similar. For these anomalies the contribution of the initial values ($\delta^2$H$_{ini}$; Figure 5.25 b) is smaller and the contribution of the changes along the trajectories ($\Delta \delta^2$H; Figure 5.25 c) is larger than for the climatological $\delta^2$H$_{fin}$. The changes along the trajectories on average account for 68% and 77% of the daily and monthly anomalies, respectively, in the whole domain, and for 85% and 95% in the southern half. This means that they are mainly responsible for the observed variability on the daily and monthly time scale. The anomalies resulting from the changes along the trajectories can again be separated into the different processes (Figures 5.26 and 5.27). Note that for the processes that increase the moisture content of the air parcels, a positive anomaly can mean that either $\delta^2$H in the moisture added by the process was higher, or the fraction of moisture added by the process was smaller (or both, and vice versa for negative anomalies). This is due to the multiplication of $\delta^2$H with $q_{fin}$ at each time step (see Equation 5.8). Since $\delta^2$H is (almost) always negative, multiplication of $\delta^2$H with a smaller positive number (smaller $q_{fin}$) results in a less negative number (positive anomaly). For the processes that decrease the moisture content of the air parcels (when $q_{fin}$ stays constant), a positive anomaly can mean less decrease
or more increase of $\delta^2$H or a smaller fraction of $q_{\text{fin}}$ contained in the air parcels during the time steps assigned to the process, and vice versa. A more detailed mathematical explanation is given in Appendix A.3. Thus, the difference in the total fraction of moisture explained by the processes $q_{\text{exp}}^k$ indicates which of the two cases prevailed. The contributions of the different processes show a large spatial variability. Over the ocean the main reason for the higher $\delta^2$H are the higher $\delta^2$H during evaporation from the ocean both on the daily and monthly time scale (Figures 5.26 d and 5.27 d). On

Figure 5.25: Difference in the $\delta^2$H anomalies with respect to the monthly climatology between the high and low anomaly days (left) and months (right) at each grid point. The top row shows the mean $\delta^2$H in water vapour on the first, third and fifth lowest model level, the middle and bottom rows show the weighted contributions of the initial values and the changes along the trajectories, respectively. The numbers show the mean contribution of each term to $\delta^2$H$_{\text{fin}}$, and the contours show the difference in the percentage of moisture explained by each term ($q_{\text{exp}}$). Stippling indicates areas where $p < 0.01$. Note the different colour scales between the left and right hand side.
the daily time scale, evaporation from the ocean leads to a negative anomaly at the coast of the Mediterranean, Black Sea, and partly the North Atlantic. Here this is due to the higher fraction of moisture coming from the ocean on days and months with high $\delta^2\text{H}$ (and not due to lower $\delta^2\text{H}$, as can be seen from the difference in $q^k_{\text{exp}}$ from ocean evaporation). For the same areas (except the coast of the Black Sea) the fraction of moisture coming from mixing with moister air is lower, resulting in a positive anomaly for this process (Figure 5.26f), which compensates the negative anomaly from evaporation from the ocean. At the Black Sea the negative anomaly is compensated by

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_26.png}
\caption{Contributions of the processes to the daily $\Delta \delta^2\text{H}$ in Figure 5.25c. The numbers show the mean contribution of each process, and the contours show the difference in the percentage of moisture explained by each process ($q^k_{\text{exp}}$; see Equations 5.13 and 5.14) between the high and low anomaly days. Stippling indicates areas where $p < 0.01$. Note the different colour scales for $q^k_{\text{exp}}$ between the left and right hand side.}
\end{figure}
evaporation from land (Figure 5.26 b). Hence there was more evaporation from the ocean and less mixing and evaporation from land on days with high $\delta^2$H. Over the rest of Europe the high $\delta^2$H anomalies are a mixture of contributions from mixed phase and liquid cloud formation (less mixed phase and more liquid clouds), evaporation from land and ocean, and mixing with moister air. Noteworthy is, especially, the large contribution of mixed phase clouds to the $\delta^2$H anomalies (on average 16%; Figure 5.26 c) in comparison to their small influence on the climatological $\delta^2$H (on average 3%; see Figure 5.22 c). Mixing with drier air is relevant over the Iberian peninsula and North Africa. Ice clouds have no influence, and the time steps for which no process was

![Figure 5.27: Contributions of the processes to the monthly $\Delta \delta^2$H in Figure 5.25 c. The numbers show the mean contribution of each process, and the contours show the difference in the percentage of moisture explained by each process ($q^k_{\text{exp}}$; see Equations 5.13 and 5.14) between the high and low anomaly months. Stippling indicates areas where $p < 0.01$. Note the different colour scales for $q^k_{\text{exp}}$ between the left and right hand side.](image)
assigned contribute slightly positively to the anomalies over Europe. On the monthly
time scale the patterns look similar, but there is a more negative contribution of land
evaporation and a more positive contribution of mixing with moister air over Europe
(Figure 5.27 b,f). Furthermore, the negative anomaly from ocean evaporation at the
coasts is weaker on the monthly than on the daily time scale (Figure 5.27 d).
Figure 5.28 shows the difference between the high and low anomaly composites
for deuterium excess. Here the difference is larger over ocean than over land (Fig-

![Figure 5.28](image)

**Figure 5.28:** Difference in the deuterium excess anomalies with respect to the monthly clima-
tology between the high and low anomaly days (left) and months (right) at each grid point. The
top row shows the mean deuterium excess in water vapour on the first, third and fifth lowest
model level, the middle and bottom rows show the weighted contributions of the initial values
and the changes along the trajectories, respectively. The numbers show the mean contribu-
tion of each term to $d_{\text{fin}}$, and the contours show the difference in the percentage of moisture
explained by each term ($q_{\text{exp}}$). Stippling indicates areas where $p < 0.01$. Note the different
colour scales between the left and right hand side.
ure 5.28 a), especially for the daily anomalies, hence, the variability is higher over the ocean. The initial values contribute slightly negatively to both the daily and monthly deuterium excess anomalies. As a consequence, the changes along the trajectories contribute with more than 100% to the anomalies, and are therefore able to fully explain the daily and monthly deuterium excess variability.

Separation of these changes into the different processes shows less spatial variability than for the $\delta^{2}H$ anomalies, and a clear dominance of one process, which is evaporation from the ocean (Figures 5.29 and 5.30). It contributes with 71% and 68% on average to the daily and monthly anomalies, respectively, and with 81% and 79% over a b c d e f g h

\(q_{\text{exp}}^{k}\) (see Equations 5.13 and 5.14) between the high and low anomaly days. Stippling indicates areas where \(p < 0.01\). Note the different colour scales for \(q_{\text{exp}}^{k}\) between the left and right hand side.

**Figure 5.29:** Contributions of the processes to the daily $\Delta d$ in Figure 5.28 c. The contours show the difference in the percentage of moisture explained by each process.
the ocean. This is primarily due to the larger moisture input from the ocean (positive $q^{k}_{\text{exp}}$ difference in Figures 5.29d and 5.30d) due to stronger evaporation, which is likely related to the lower amount of liquid clouds (and consequently precipitation) over the ocean (negative $q^{k}_{\text{exp}}$ difference in Figures 5.29a and 5.30a) leading to a lower relative humidity. Over land the formation of liquid clouds, evaporation from land, and mixing with moister air are similarly important as evaporation from the ocean. Mixed phase clouds, ice clouds, mixing with drier air, and the time steps, for which no process is assigned, are of minor importance for deuterium excess variability.

Figure 5.30: Contributions of the processes to the monthly $\Delta d$ in Figure 5.28c. The contours show the difference in the moisture explained by each process ($q^{k}_{\text{exp}}$; see Equations 5.13 and 5.14) between the high and low anomaly months. Stippling indicates areas where $p < 0.01$. Note the different colour scales for $q^{k}_{\text{exp}}$ between the left and right hand side.
5.3.4 Extratropical cyclones and fronts

Frequencies

Figure 5.31 shows the mean cyclone frequencies in the COSMOiso simulation for the four seasons during the years 2002–2011. In all seasons the frequencies are higher over the Atlantic than over continental Europe, which means that most cyclones coming from the storm track and entering the model domain from the west decayed before moving over land. At the boundaries of the model domain the cyclones are more difficult to identify, which is why the frequencies generally decrease towards the boundaries. In summer, North Atlantic cyclones tend to arrive in Europe more to the North than in the other seasons, resulting in higher frequencies over the United Kingdom. Apart from the main storm track, cyclones often appear in the Tyrrhenian and Adriatic Sea and in the eastern Mediterranean, with peak values (> 12%) occurring in winter. Furthermore, a very high cyclone frequency (> 32%) can be found in the eastern part of the Black Sea in summer (a bit lower also in autumn). This could be connected to mesoscale convective systems developing there. Except for this high frequency, the seasonal cyclone frequencies agree well with the cyclone climatology from Wernli and Schwierz (2006), which is based on the ERA40 dataset (Uppala et al., 2005).

Fronts occur most often over the North Atlantic, with the highest frequencies (> 26%) in summer and autumn (Figure 5.32). About half of them also move over the continent, which results in high frequencies over northeastern Europe. In southwestern Europe and the Mediterranean the fronts appear more rarely, or, since the orography can

![Figure 5.31: Seasonal cyclone frequency in the COSMOiso simulation (in %).](image-url)
disturb the gradients, are not detected by the objective front identification algorithm. The frontal climatology from Schemm et al. (2015), which is based on the ERAinterim dataset (Dee et al., 2011), shows higher frequencies in winter than in summer over the Atlantic (i.e., opposite to here), but they also found more fronts over Europe and the Mediterranean in summer than in winter (spring and autumn climatologies are not included in their article).

Cyclone anomalies

Figure 5.33 shows the temperature, precipitation, and evaporation anomalies of air masses associated with a cyclone compared to air masses not associated with a cyclone, both from the Eulerian and Lagrangian perspective (as explained in Section 5.2.4) during the years 2002–2011. Stippling again indicates where the anomalies are significant according to a two-sided t-test. The anomalies for each season (shown in Figures C.1–C.4) are similar to the annual anomalies. Not surprisingly, the (Eulerian) precipitation amount is higher in almost the entire model domain when a cyclone is present (Figure 5.33 a). The largest anomalies can be found over the Alps and Balkan mountains, where the cyclones advect moist air from the Mediterranean, which is then orographically lifted. Cyclones also generally lead to higher temperatures (except over mountains and the Mediterranean), and stronger evaporation, although these anomalies are mostly not statistically significant. The (Lagrangian) rainout of the trajectories associated with a cyclone is larger over the Mediterranean and smaller over the Atlantic compared to trajectories not associated with a cyclone (Figure 5.33 b).
Figure 5.33: Anomalies of temperature (left), precipitation / rainout (middle), and evaporation (right) of air masses associated with a cyclone compared to air masses not associated with a cyclone from (a) the Eulerian, and (b) the Lagrangian perspective. The Lagrangian anomaly of rainout is given as a ratio, all other variables are given as differences. The Eulerian precipitation and evaporation are 1 hourly accumulated. Stippling indicates areas where $p < 0.01$.

As already mentioned in Section 5.3.2, the values for rainout over the Atlantic should not be overinterpreted since most of the trajectories entered the model domain only shortly before their arrival. The trajectories associated with a cyclone also experience more evaporation from ocean and land (defined as $q_{exp}$ from ocean plus land evaporation), while their integrated temperature ($T_L$; see Section 5.2.3) is similar to the trajectories not associated with a cyclone. The corresponding isotope anomalies are shown in Figure 5.34 (and in Figures C.5–C.8 separately for each season). In the presence of cyclones the $\delta^{2}H$ values in precipitation and vapour are lower (Figure 5.34 a,b, left), which is likely due to the higher precipitation amount seen in Figure 5.33 a (i.e., the amount effect). The temperature effect would mostly lead to higher $\delta^{2}H$ (due to the higher temperatures), and is therefore not valid for cyclones. The lowest $\delta^{2}H$ anomalies in vapour can be found over the Alps and the Balkan mountains, which nicely corresponds to the highest precipitation anomalies in Figure 5.33 a. This is where the air parcels experience strong rainout due to orographic lifting and become progressively depleted in $\delta^{2}H$. Also most of the trajectories associated with a cyclone have a significantly lower $\delta^{2}H$ than trajectories not associated with a cyclone (Figure 5.34 c, left). Exceptions are the trajectories arriving in the East of the domain, over North Africa, and part of the Mediterranean.
Figure 5.34: Anomalies of $\delta^2$H (left) and deuterium excess (right) of air masses associated with a cyclone compared to air masses not associated with a cyclone from (a,b) the Eulerian, and (c) the Lagrangian perspective. The Eulerian $\delta^2$H and deuterium excess values are shown in precipitation (a), and water vapour (b). Stippling indicates areas where $p < 0.01$.

The deuterium excess in precipitation and vapour is higher when cyclones are present (Figure 5.34 a,b, right), in accordance with the stronger evaporation seen in Figure 5.33 a. The highest deuterium excess anomalies in vapour can again be found over the Alps and Balkan mountains. This may be due advection of air masses from the Mediterranean by the cyclones, which typically have high deuterium excess values (see Figure 5.21). The deuterium excess in the trajectories associated with a cyclone is higher over the Atlantic and lower over the Mediterranean and Black Sea (Figure 5.34 c, right). However, the differences are barely significant.

**Front anomalies**

Figure 5.35 shows the temperature, precipitation, and evaporation anomalies of air masses associated with a front compared to air masses not associated with a front,
again from the Eulerian and Lagrangian perspective. All three variables are generally higher when a front is present. The signal is dominated by the summer and autumn values, since fronts occur most often in these two seasons (cf. Figure 5.32). However, it is not primarily due to seasonality, since the patterns look similar if the seasons are considered separately (shown in Figures C.9–C.12). The generally higher temperature (both from the Eulerian and Lagrangian perspective) indicates that the identified frontal air masses are predominantly from the warm sector.

The corresponding isotope anomalies are shown in Figure 5.36 (and in Figures C.13–C.16 separately for each season). In the presence of fronts the $\delta^2\text{H}$ values in precipitation and vapour are higher (Figure 5.36 a,b, left). Hence, in contrast to the cyclones, the temperature effect holds for the fronts, while the amount effect is not valid, as it would lead to lower $\delta^2\text{H}$. This is also true for the trajectories (Figure 5.36 c, left), which generally have a higher $\delta^2\text{H}$ if they are associated with a front.

The deuterium excess in precipitation and vapour is lower when fronts are present over the North Atlantic and northwestern Europe, and higher over southeastern Europe, the Mediterranean and North Africa (Figure 5.36 a,b, right). This is likely connected to the evaporation anomalies in Figure 5.35 a. Also the trajectories associated with a front generally have a lower deuterium excess than trajectories not associated with a front.

![Figure 5.35](image.png)

**Figure 5.35:** Anomalies of temperature (left), precipitation / rainout (middle), and evaporation (right) of air masses associated with a front compared to air masses not associated with a front from (a) the Eulerian, and (b) the Lagrangian perspective. The Lagrangian anomaly of rainout is given as a ratio, all other variables are given as differences. The Eulerian precipitation and evaporation are 1 hourly accumulated. Stippling indicates areas where $p < 0.01$. 


Figure 5.36: Anomalies of $\delta^2$H (left) and deuterium excess (right) of air masses associated with a front compared to air masses not associated with a front from (a,b) the Eulerian, and (c) the Lagrangian perspective. The Eulerian $\delta^2$H and deuterium excess values are shown in precipitation (a), and water vapour (b). Stippling indicates areas where $p < 0.01$.

(Figure 5.36 c, right). The lowest anomaly can be found over the North Atlantic, west of the United Kingdom, where the rainout anomaly of the trajectories is highest (cf. Figure 5.35 b). As shown in Section 5.3.3, cloud formation processes can sometimes decrease the deuterium excess, however, such a strong effect seems unrealistic, even if all clouds that formed in the air parcels were ice clouds involving nonequilibrium effects.

5.4 Discussion

According to the evaluation with the GNIP measurements (Section 5.3.1), nesting COSMOiso within the GCMs (IsoGSM and ECHAMwiso) led to an improvement of the simulations. Furthermore, COSMOiso produced the best results, when it was
forced with ECHAMwiso boundary data and used external soil isotope concentrations and the wind speed independent formulation of the nonequilibrium fractionation factor. ECHAMwiso alone also performed better than IsoGSM, although both simulations were nudged to reanalysis data. The main reason for this is probably the higher resolution that was used for the ECHAMwiso simulation than for the IsoGSM simulation (T106 compared to T62). The COSMOiso simulations forced with ECHAMwiso additionally benefited from the consistency between the isotope fields and standard atmospheric and surface fields, while the others used the isotope fields from IsoGSM and the standard fields from ERAinterim reanalyses. More surprising was the slightly worse performance of the COSMOiso simulations coupled to TERRAiso, since the physical representation of the feedbacks between the isotopes in the soil and in the atmosphere was expected to produce more realistic results than prescribed external soil isotope concentrations. However, the parameterisations used in TERRAiso involve uncertainties, which have not been extensively tested yet, as the model is quite new. Furthermore, experiments performed with a stand-alone version of TERRAiso indicated that the assumption of nonfractionating soil water (used in the case of external data) is legitimate on long time scales (≥ months), since the enrichment of the upper soil layers through evaporation compensates the fractionation effect on vapour, leading to similar isotope ratios as if no fractionation occurred (F. Aemiseegger, pers. comm., 2016). The better representation of deuterium excess in the simulations using the wind speed independent nonequilibrium fractionation factor during evaporation suggests that the impact of wind speed on deuterium excess is negligible. Part of the difference between the two formulations, however, is also the absolute strength of nonequilibrium fractionation, which is higher in the case of the wind speed independent formulation. Thus, the underestimation of deuterium excess by the classical formulation could also be due to generally too weak nonequilibrium fractionation. Further tests and measurements are needed to clarify the role of wind speed.

As shown in Section 5.3.2, the correlation between local temperature and $\delta^2$H in near-surface water vapour was mostly positive and strong, consistent with previous studies (e.g., Jacob and Sonntag, 1991; Rozanski et al., 1992; Aemiseegger, 2013; Bastrikov et al., 2014). Exceptions were the southwestern part of the Iberian peninsula and North Africa where no significant correlation could be found (except on the monthly time scale for North Africa). Weak correlations between temperature and $\delta^2$H or $\delta^{18}$O are often observed at coastal stations (e.g., Rozanski et al., 1993; Posmentier et al., 2004; Vreča et al., 2006) and explained by, e.g., larger influence of marine air masses, smaller variations of temperature, or more variable precipitation regimes compared to continental stations. The decomposition of the $\delta^2$H anomalies into the different processes in Section 5.3.3 indicated a positive contribution of liquid cloud formation and
mixing with drier air particularly over North Africa and the Iberian peninsula, meaning that there was less depletion by these two processes on days and months with high $\delta^2$H. This may be a sign for less rainout and a larger influence of moist (marine) air masses, which could contribute to the high $\delta^2$H values unrelated to temperature. Rainout ($P_L$ as defined in Section 5.2.3) was also negatively correlated with $\delta^2$H, but only on the monthly time scale, whereas on the hourly and daily time scale no significant correlation was found. The reason for this may be that the definition of rainout applied here is oversimplified, since it does not account for the chronological order of moisture losses and uptakes. For example, an air parcel that lost all its moisture in the beginning and then took up new moisture towards the end could have the same rainout as an air parcel that took up moisture in the beginning and then continuously lost moisture on the way, but they would most likely have a very different isotopic composition. This different order might average out on long time scales, resulting in a more reliable estimate of rainout and therefore a better correlation with $\delta^2$H.

Furthermore, a strong negative correlation between local relative humidity and deuterium excess was found over the ocean on all time scales, which is in agreement with observations from Gat et al. (2003), Uemura et al. (2008), and Steen-Larsen et al. (2014). Over land the correlation was weak or even negative (on the yearly time scale). Aemisegger et al. (2014) found similar weak correlations for hourly deuterium excess values with local relative humidity in Switzerland, and stronger negative correlations with relative humidity at the moisture sources. This latter finding is supported by our results for the correlations between deuterium excess and the Lagrangian relative humidity, which was diagnosed in a similar way. This indicates that relative humidity over the ocean is the primary factor controlling the deuterium excess in atmospheric moisture, as suggested by Pfahl and Sodemann (2014). The correlation of deuterium excess and surface temperature was mostly negative, and thus exactly opposite to the assumption made by many paleoclimatic studies that used deuterium excess as a proxy for the sea surface temperature at the moisture sources (Barlow et al., 1993; Vimeux et al., 1999; Stenni et al., 2001; Uemura et al., 2012). The negative correlation most likely resulted from the crosscorrelation of surface temperature and relative humidity (as also suggested by Aemisegger et al., 2014). However, it has to be noted that due to the complexity of nonequilibrium fractionation, deuterium excess is more difficult to reproduce for COSMOiso than $\delta^2$H or $\delta^{18}$O alone, and the simulated values were sometimes very different from measurements. Therefore the quantitative relations between deuterium excess and meteorological variables should be taken with caution.

The decomposition of $\delta^2$H and deuterium excess into the different processes in Section 5.3.3 showed that the moisture increasing processes (ocean evaporation, land
evaporation, mixing with moister air) mainly determine $\delta^{2}H$ and deuterium excess in water vapour at the lowest model levels, while the moisture decreasing processes (formation of liquid clouds, mixed phase clouds, ice clouds and mixing with drier air) had smaller contributions, although some of them (e.g., the formation of mixed phase clouds) were important for the variability. In the current setting with the starting points of the backward trajectories at low levels, all air parcels descend towards the end, while no air parcel can ascend by construction (except those having their starting point on a mountain). This means that they tend to take up moisture towards the end, which overwrites previous signals from other processes. This may explain why the moisture increasing processes are more important than the moisture decreasing processes. It would be interesting to see how the results would change for trajectories started from higher levels.

In Section 5.3.4, the isotopic composition of air masses associated with an extratropical cyclone or front were compared to the isotopic composition of air masses not associated with an extratropical cyclone or front. So far, cyclones and fronts have mainly been studied by considering the temporal evolution of $\delta^{2}H$ and deuterium excess during individual cyclone or front passages (e.g., Rindsberger et al., 1990; Celle-Jeanton et al., 2004; Aemisegger et al., 2015). However, their long-term imprint on the isotope signals in water vapour and precipitation has not been quantified yet. Our results showed that extratropical cyclones generally lead to lower $\delta^{2}H$ and higher deuterium excess in water vapour and precipitation, while fronts have the opposite effect. The lower $\delta^{2}H$ in the cyclones could be attributed to depletion due to rainout, and the higher deuterium excess to advection from the Mediterranean Sea. The signal of the fronts may partially be explained by assuming the air masses mainly belonged to the warm sector. Since the warm sector is in between the warm and the cold front it is more likely for an air parcel to be close to a front (i.e., identified as associated with a front), if it is in the warm sector, than if it is in the cold sector behind the cold front. In a future study it would make sense to distinguish between warm sector and cold sector (or warm front and cold front). However, the objective identification and distinction between warm and cold fronts is difficult over orography, which means that the model domain would need to be shifted to a pure ocean surface (e.g., the North Atlantic).

### 5.5 Conclusions

This chapter has evaluated climatological simulations of stable water isotopes over Europe from IsoGSM, ECHAMwiso and different setups of COSMOiso nested within IsoGSM or ECHAMwiso, and investigated processes and meteorological variables responsible for isotopic variability on the daily to yearly time scale. In addition to the Eu-
lerian perspective considering local variables, a Lagrangian perspective was adopted following individual air parcels along backward trajectories.

The evaluation of the models with GNIP data showed that the best results were produced by COSMOiso, when it used input data from ECHAMwiso, external soil isotope concentrations, and the wind speed independent formulation of the nonequilibrium fractionation factor during ocean evaporation. This setup was used to investigate the influence of weather systems on isotopic variability, which led to the following results:

1. $\delta^2H$ in near-surface vapour is positively correlated with temperature on the daily, monthly, and yearly time scale, except over North Africa and the southwestern part of the Iberian peninsula. $\delta^2H$ is negatively correlated with precipitation amount over the ocean, but unrelated to precipitation amount over land. There it reflects the rainout along the trajectories. Deuterium excess is almost everywhere strongly negatively correlated with relative humidity at the moisture sources on the daily, monthly, and yearly time scale, and weakly negatively correlated with sea surface temperature at the moisture sources.

2. Over the ocean, evaporation from the ocean is the primary factor controlling $\delta^2H$ and deuterium excess in water vapour at low levels. Over land, evaporation from land and mixing with moister air are similarly important. Liquid and mixed phase cloud formation contribute to the variability of $\delta^2H$ and deuterium excess, especially over continental Europe.

3. Extratropical cyclones are generally associated with lower $\delta^2H$ and higher deuterium excess values. The largest impacts can be observed over the Alps and the Balkan mountains, and in the Atlantic and Mediterranean. The low $\delta^2H$ values are mainly caused by depletion through rainout. Fronts have the opposite effect with higher $\delta^2H$ and lower deuterium excess (except in the Mediterranean, where deuterium excess values are higher). This is probably linked to the signal of warm sectors.
Chapter 6

Conclusions and outlook

Stable water isotopes are powerful natural tracers of moisture in the atmosphere, and a valuable means for improving our understanding of the water cycle. However, the complex interactions of processes involving isotopic fractionation often make interpretations of isotope measurements difficult. This thesis has investigated fractionation processes with the help of different numerical modelling simulations, and tried to disentangle the mechanisms responsible for hourly to seasonal isotopic variability, with a focus on Europe. In this chapter, the main findings are summarised, and potential future research questions are suggested.

6.1 Exponential deuterium excess

In Chapter 3, a simple Rayleigh model was used to simulate deuterium excess in moist adiabatically ascending air parcels, and three experiments with different fractionation factors were performed, which allowed quantifying the impact of three effects on the deuterium excess in the air parcels: (1) the nonequilibrium effect during ice and mixed phase cloud formation, (2) the temperature effect due to the temperature dependence of the equilibrium fractionation factors, and (3) the nonlinear effect of the δ scale, which implies that the change of δ depends, apart from the fractionation factor, also on δ itself, being smaller for more negative δ values. The results showed that in air parcels, which have experienced a lot of rainout (i.e., typically at high latitudes or altitudes), the nonlinear effect of the δ scale dominates the other two effects, and can lead to a large increase of the deuterium excess. This means that in these air parcels the deuterium excess to a large extent reflects an artefact of its definition, which overwrites the signals from the moisture sources that are often thought to be the main factor of influence on deuterium excess (e.g., Vimeux et al., 2001; Masson-Delmotte et al., 2005; Kopec et al., 2016).

We proposed an alternative definition of the deuterium excess (the exponential deuterium excess), which is based on the logarithmic scale, similarly to the $^{17}\text{O}$ excess,
and therefore unaffected by the nonlinear effect of the $\delta$ scale. In the Rayleigh model the exponential deuterium excess is independent of the $\delta$ values, and stays nearly constant in absence of the nonequilibrium and temperature effect, meaning that the initial signal from moisture sources is preserved. The temperature effect can lead to more negative or more positive values of the exponential deuterium excess in the remaining vapour, depending on the temperature of the air parcels, while the nonequilibrium effect always leads to more negative values, due to the faster diffusion of HD$^{16}$O to the ice crystals compared to H$_2^{18}$O (Jouzel and Merlivat, 1984). However, the exponential deuterium excess has limitations related to the mixing of air parcels, since it is defined as a ratio instead of a difference. In contrast to the standard deuterium excess, the exponential deuterium excess of a mixture can be different from the linear combination of the individual components.

Thus, the two deuterium excess definitions have different benefits and limitations, while none of them is a pure measure for nonequilibrium effects. The exponential deuterium excess has an advantage for processes involving Rayleigh condensation, but whether it would be a good alternative to the standard deuterium excess also in general is still an open question. Further tests are needed to quantify its sensitivity to mixing and other processes occurring in the water cycle. In the 10-year simulation with COSMOiso presented in Chapter 5, the mean values of the two deuterium excess definitions in water vapour look very similar, except for an offset of $\sim 7^\circ_{\text{o}}$ (Figure 6.1). The difference between the two is larger over the Mediterranean and smaller over continental Europe, especially over the Alps, where air parcels usually experience strong rainout due to orographic lifting. This may be a region where the nonlinear effect of the $\delta$ scale leads to artificially high values of the standard deuterium excess, and the exponential deuterium excess could prove to be a helpful complementary parameter.
6.2 Isotope models and measurements

In Chapter 5, climatological simulations of stable water isotopes over Europe with IsoGSM, ECHAMwiso, and different setups of COSMOiso were validated against measurements of the Global Network of Isotopes in Precipitation (GNIP) for the years 2002–2011. The COSMOiso simulations showed an improved performance compared to IsoGSM and ECHAMwiso, underlining the added value of simulating stable water isotopes with high horizontal resolutions. The mean and variability of $\delta^2$H was remarkably well reproduced by COSMOiso, while deuterium excess was more problematic. This could be due to deficiencies in the parameterisation of isotope processes in COSMOiso, physical processes in COSMO itself, or, not least, uncertainties in the measurements. An additional model evaluation with a different observational dataset (ideally with a higher temporal resolution than the GNIP measurements) would be helpful to identify the main reasons. One option are ground- or aircraft-based in situ measurements (e.g., Aemisegger et al., 2014; Sodemann et al., 2016). However, they typically cover a limited area and time range, and are therefore more suited for validating model simulations of single events. In recent years, remote sensing techniques for measuring stable water isotopes have become increasingly available (e.g., Schneider et al., 2006; Worden et al., 2006; Lacour et al., 2012). They offer continuous daily observations with a large spatial coverage. So far they only measure $\delta^2$H, and therefore cannot provide information on deuterium excess. Nevertheless, they present a unique opportunity for validating simulations of isotopes in free tropospheric water vapour, and can help constraining parameterisations applied in the models (Risi et al., 2012) and detecting compensating errors which are not visible in the moisture, temperature or pressure fields (Galewsky et al., 2016). Since COSMOiso is able to resolve the small-scale structures that are measured by remote sensing techniques, it is a very suitable model for investigating and evaluating stable water isotope processes in combination with these measurements.

6.3 Fractionation and advection of isotopes

In Chapter 4, COSMOiso was used in an idealised baroclinic channel framework to simulate an isolated extratropical cyclone and quantify its impacts on fractionation and advection of isotopes. This was done by defining different initial isotope fields and selectively switching off certain fractionation processes in the model. The results showed that the nonlinear effect of the $\delta$ scale on $\delta^2$H, in contrast to the deuterium excess (see above), is small, and therefore the isotope signal of the cyclone could be decomposed into the contributions from different processes. The descending trend
of $\delta^2H$ observed in many measurement campaigns of cold frontal passages could be attributed to the advection of more depleted air masses behind the cold front, while fractionation processes (progressive depletion during rainout and below cloud interactions), were responsible for a V-shaped trend of $\delta^2H$. The 10-year realistic simulation presented in Chapter 5 showed that extratropical cyclones in Europe generally lead to lower $\delta^2H$ in water vapour and precipitation, which likely results from a combination of these processes. Fronts led to the opposite signal, probably due to the prevailing signal of warm air advection. The method applied in this simulation for attributing air masses to extratropical cyclones and fronts was rather straightforward, and could be improved in the future, for example by introducing an altitude limit and/or a minimum sea level pressure criterion for the cyclones, or distinguishing between cold and warm fronts.

For quantifying the impact of the fractionation processes from a climatological perspective, fractionation can be switched off also in the 10-year simulations, although not completely, since they are still contained in the boundary conditions (unless the GCM simulations were rerun as well). As an example, Figure 6.2 shows $\delta^2H$ and deuterium excess in a 5-year simulation (2002–2006) with the same setup as the simulation used for the analysis in Chapter 5, but the impact of below cloud interactions on isotopes switched off inside the COSMOiso domain. The difference between the two simulations indicates how fractionation during rain drop evaporation and equilibration generally increases $\delta^2H$ and decreases deuterium excess in precipitation (in accordance with the results from the idealised cyclone for $\delta^2H$). This would be an interesting approach to pursue further, and maybe repeat for other fractionation processes (e.g., cloud formation).

Similar experiments as for $\delta^2H$ in the idealised baroclinic channel can also be performed for deuterium excess. However, nonlinearities have a large impact on deuterium excess, and a decomposition into the different processes would not be possible in the same way as for $\delta^2H$. Here the exponential deuterium excess definition might be a good alternative, since it is independent of the $\delta$ values.

### 6.4 Hourly to seasonal isotopic variability

The main focus of Chapter 5 was the influence of meteorological variables and processes on stable water isotopes, which was analysed in a realistic 10-year simulation over Europe with the COSMOiso setup that performed best compared to the GNIP measurements. Correlations of $\delta^2H$ and deuterium excess with temperature, precipitation amount, relative humidity, and surface temperature highlighted the important
role of temperature for the variability of $\delta^2$H, especially on the seasonal time scale. Relative humidity at the moisture sources proved to be the main driver of deuterium excess in most locations. Due to the short time period of 10 years, we neglected interannual variability in this simulation. Yet, the increasing strength of the correlations with longer time scales suggests that these relations also hold on interannual time scales and underlined that isotopes are useful proxies of past climate variability. Nevertheless, it would be interesting to extend the simulation to a longer time period (e.g., 30 years) to gain more insight into interannual isotopic variability. Furthermore, a principle component analysis of $\delta^2$H and deuterium excess over Europe, similar as in Rimbu et al. (2016) for central Greenland isotope records, may be helpful for better understanding the main modes of isotopic variability and their relation to meteorological variables.

In the second part of Chapter 5 we presented a Lagrangian method for quantifying the impact of different processes on $\delta^2$H and deuterium excess along trajectories, which revealed that the climatological mean $\delta^2$H and deuterium excess in near-surface water vapour is mainly determined by evaporation from the ocean, evaporation from land, and mixing with moister air, while cloud formation processes were found to be important for the variability of $\delta^2$H and deuterium excess over continental Europe. The
dominance of processes that increase the moisture content of the air parcels is related to the setup of the analysis, since trajectories have been selected that arrived at low levels and therefore tended to take up moisture towards the end. The same method could be applied to trajectories arriving at higher levels (e.g., where clouds form), which would presumably lead to different results. Furthermore, the analysis could be extended by differentiating between different seasons or years. Also for this a longer simulation time would be useful. Additionally, the model domain could be shifted to a different area, e.g., the subtropics or tropics, where isotopic variability is governed by different processes.

6.5 Final remarks

Weather systems comprise a large number of processes involving fractionation, and thereby shape the isotopic composition of water vapour and precipitation. Understanding the complex interactions of these processes and their impact on isotopic variability is essential for fully exploring the potential of stable water isotopes as tracers of the atmospheric water cycle. Numerical models equipped with stable water isotopes are a valuable tool for studying fractionation processes and help in the interpretation of isotope measurements, as they fill the gap between theoretical concepts and reality. The climatological perspective obtained from GCMs can be complemented by a more process-oriented approach from limited area models, which are able to resolve the small spatial and temporal scales, on which isotope processes occur. In combination with systematic observations of stable water isotopes, these models present a promising opportunity for investigating isotopic variability in water vapour and precipitation and in this way improving our understanding of the atmospheric water cycle.
Appendix A

Mathematical explanations

A.1 Derivation of the Rayleigh condensation equation

The Rayleigh condensation equation (Equation 1.5) can be derived as follows (following Zeebe and Wolf-Gladrow, 2001). At time $t = 0$ the water vapour consists of a number of particles of the abundant isotope $N_1^0$ and a number of particles of the rare isotope $N_2^0$. At time $t > 0$ the numbers are reduced to $N_1$ and $N_2$ (after water has condensed from the vapour). The number of particles in the condensate are denoted as $n_1$ and $n_2$. The isotope ratios $R^0$ and $R$ in the (remaining) vapour can be determined through:

\[ R = \frac{N_2}{N_1} \]  \hspace{1cm} (A.1a)

\[ R^0 = \frac{N_2^0}{N_1^0} \]  \hspace{1cm} (A.1b)

For an infinitesimal number of particles $dn$ removed from the vapour the ratio in the instantaneous condensate is given by the ratio in the vapour times the equilibrium fractionation factor between liquid and vapour $\alpha_{lv}$:

\[ \frac{dn_2}{dn_1} = \alpha_{lv} \frac{N_2}{N_1} \]  \hspace{1cm} (A.2)

Since mass is conserved we have:

\[ N_1 + n_1 = const. \]  \hspace{1cm} (A.3a)

\[ N_2 + n_2 = const. \]  \hspace{1cm} (A.3b)
and thus

\[ dN_1 = -dn_1 \quad (A.4a) \]
\[ dN_2 = -dn_2 \quad (A.4b) \]

Equation A.2 can therefore also be written as

\[ \frac{dN_2}{dN_1} = \alpha^{l/v} \frac{N_2}{N_1} \quad (A.5) \]

which can be solved by integration:

\[ \int_{N_2^0}^{N_2} \frac{dN_2'}{N_2'} = \alpha^{l/v} \int_{N_1^0}^{N_1} \frac{dN_1'}{N_1'} \quad (A.6) \]

This results in:

\[ \ln \left( \frac{N_2}{N_2^0} \right) = \alpha^{l/v} \cdot \ln \left( \frac{N_1}{N_1^0} \right) \quad (A.7) \]

and

\[ \left( \frac{N_2}{N_2^0} \right) = \left( \frac{N_1}{N_1^0} \right)^{\alpha^{l/v}} \quad (A.8) \]

which can also be written as:

\[ \left( \frac{N_2}{N_2^0} \right) = \left( \frac{N_1}{N_1^0} \right) \left( \frac{N_1}{N_1^0} \right)^{\alpha^{l/v}-1} \quad (A.9) \]

Since \( N_1 \gg N_2 \) the fraction of the remaining vapour \( f = \frac{N_1+N_2}{N_1^0+N_2^0} \) can be approximated by \( f = \frac{N_1}{N_1^0} \).
Hence, with $\frac{R}{R^0} = \frac{N_2/N_0}{N_2^0/N_0^0}$, this results in:

$$\frac{R}{R^0} = f\alpha^{\nu-1}$$  \hspace{1cm} (A.10)

### A.2 The mixing effect

This section explains the mathematical concept behind the mixing effect on the exponential deuterium excess in more detail. We consider again two air parcels 1 and 2, which mix with a relative moisture fraction of $p$ and $q = 1 - p$, respectively. The total deuterium excess of both air parcels $\tilde{d}_{\text{mix}}$ and the linear combination $\tilde{d}_{\text{lin}}$ can be expressed in a simplified form as:

$$\tilde{d}_{\text{mix}} = \frac{pa + qb}{(px + qy)^m}$$  \hspace{1cm} (A.11)

$$\tilde{d}_{\text{lin}} = \frac{pa}{x^m} + \frac{qb}{y^m}$$  \hspace{1cm} (A.12)

with $a = R^{r2}H_1$, $b = R^{r2}H_2$, $x = R^{r18}O_1$, and $y = R^{r18}O_2$.

The difference between $\tilde{d}_{\text{mix}}$ and $\tilde{d}_{\text{lin}}$ is largest if $p \approx q$, hence if the two air parcels have about the same moisture amount. There are two special cases:

- $x = y$ (or $\delta^{18}O_1 = \delta^{18}O_2$)
  In this case the difference is 0 because the denominators of $\tilde{d}_{\text{mix}}$ and $\tilde{d}_{\text{lin}}$ are equal ($(py + qy)^m = y^m$).

- $a = b$ (or $\delta^2H_1 = \delta^2H_2$)
  In this case the difference is $\leq 0$, because $c/z^m$ with $m > 0$ is a convex function of $z$. The weighted mean of a convex function (here $\tilde{d}_{\text{lin}}$) is always larger or equal to the convex function of the weighted mean (here $\tilde{d}_{\text{mix}}$), hence:

$$\frac{b}{(px + qy)^m} \leq \frac{pb}{x^m} + \frac{qb}{y^m}$$  \hspace{1cm} (A.13)

This is known as Jensen’s inequality and was proven by Jensen (1905).

The remaining cases can be separated into two groups:

- $(a - b)(x - y) < 0$, hence $\delta^2H_1 - \delta^2H_2$ has the opposite sign of $\delta^{18}O_1 - \delta^{18}O_2$ (upper left and lower right corner in Figure 3.8)
In this case the difference is always < 0, which can be shown with the following steps. From \((a - b)(x - y) < 0\) and \(m > 0\) it follows that:

\[
a(x^m - y^m) - b(x^m - y^m) < 0
\]  
(A.14)

Multiplying with \(p\) and \(q\) gives:

\[
pqa(x^m - y^m) - pqb(x^m - y^m) = pa(qx^m - qy^m) - qb(px^m - py^m) = pa(qx^m + py^m - y^m) + qb(py^m + qx^m - x^m) = py^m(pa + qb) + qx^m(pa + qb) - (py^m + qx^m) < 0
\]  
(A.15)

Dividing by \(x^m y^m\) then results in:

\[
\frac{p(pa + qb)}{x^m} + \frac{q(pa + qb)}{y^m} < \frac{pa}{x^m} + \frac{qb}{y^m} = \tilde{d}_{\text{lin}}
\]  
(A.16)

From Equation A.13 we know that:

\[
\tilde{d}_{\text{mix}} = \frac{pa + qb}{(px + qy)^m} \leq \frac{p(pa + qb)}{x^m} + \frac{q(pa + qb)}{y^m}
\]  
(A.17)

And therefore:

\[
\tilde{d}_{\text{mix}} = \frac{pa + qb}{(px + qy)^m} < \frac{pa}{x^m} + \frac{qb}{y^m} = \tilde{d}_{\text{lin}}
\]  
(A.18)

- \((a - b)(x - y) > 0\), hence \(\delta^2\text{H}_1 - \delta^2\text{H}_2\) has the same sign as \(\delta^{18}\text{O}_1 - \delta^{18}\text{O}_2\) (lower left and upper right corner in Figure 3.8)

In this case the difference can be either positive or negative. This is certainly the most frequent case describing the mixing of an enriched and a depleted air parcel with both having a potentially small deuterium excess close to 0\(^\circ\). In the extreme case the air parcels’ individual exponential deuterium excess is 0\(^\circ\), while their mixture has a positive deuterium excess.
A.3 $\delta^2 H$ anomalies

This section explains why a smaller fraction of moisture ($q_{fin}$) contained in the air parcel during moisture losses or added during moisture uptakes can lead to a positive $\Delta \delta^2 H$ anomaly. We consider one time step and two air parcels $a$ and $b$. Air parcel $a$ experiences a larger increase in $q_{fin}/q_N \cdot \delta^2 H$ ($q_{fin}/q_N \cdot \delta$ for simplicity) than air parcel $b$, hence:

$$\frac{\Delta (q \cdot \delta)^1_a}{q^N_a} > \frac{\Delta (q \cdot \delta)^1_b}{q^N_b}$$  \hspace{1cm} (A.19)

$$\frac{q^2_a \cdot \delta^2_a - q^1_a \cdot \delta^1_a}{q^N_a} > \frac{q^2_b \cdot \delta^2_b - q^1_b \cdot \delta^1_b}{q^N_b}$$  \hspace{1cm} (A.20)

$$p^2_a \cdot \delta^2_a - p^1_a \cdot \delta^1_a > p^2_b \cdot \delta^2_b - p^1_b \cdot \delta^1_b$$  \hspace{1cm} (A.21)

where $q^n$ denotes the moisture at time $n$ that is still contained in the air parcel at its arrival point, at time $N$ (usually referred to as $q_{fin}^n$), and $p$ denotes the fraction of $q^N$ contained in the air parcel at time $n$ ($p^n = q^n/q^N$).

In the case of moisture losses $p^2$ is always equal to $p^1$. Hence, Equation A.21 can be expressed as:

$$p^2_a \cdot (\delta^2_a - \delta^1_a) > p^2_b \cdot (\delta^2_b - \delta^1_b)$$  \hspace{1cm} (A.22)

Assuming $\delta^2_a - \delta^1_a = \delta^2_b - \delta^1_b$ (i.e., the same change of the $\delta$ values in both air parcels) gives:

$$p^2_a > p^2_b \text{ if } \delta^2 - \delta^1_b > 0$$  \hspace{1cm} (A.23)

$$p^2_a < p^2_b \text{ if } \delta^2 - \delta^1_b < 0$$  \hspace{1cm} (A.24)

The latter is typical for moisture losses. Hence, a smaller fraction of moisture in air parcel $a$ compared to air parcel $b$ leads to a positive anomaly (Equation A.19).

In the case of moisture uptakes $p^2$ is always larger than $p^1$, and we assume that $\delta^1_a = \delta^2_a = \delta^1_b = \delta^2_b$, hence, the $\delta$ values in the two air parcels are equal and stay constant. This simplifies Equation A.21 to:

$$p^2_a \cdot \delta^2_b - p^1_a \cdot \delta^2_b > p^2_b \cdot \delta^2_b - p^1_b \cdot \delta^2_b$$  \hspace{1cm} (A.25)

$$\delta^2_b \cdot (p^2_a - p^1_a) > \delta^2_b \cdot (p^2_b - p^1_b)$$  \hspace{1cm} (A.26)
Since the $\delta$ values are (almost) always negative this means:

$$p_a^2 - p_a^1 < p_b^2 - p_b^1 \quad \text{(A.27)}$$

Hence, a smaller fraction of moisture added to air parcel $a$ compared to air parcel $b$ leads to a positive anomaly (Equation A.19).
Appendix B

Supplement to Chapter 4

This Appendix chapter provides additional insight into several aspects of Chapter 4. Section B.1 summarises the isotope trends that have been observed in previous studies of cold front passages. Section B.2 describes the derivation of the $\delta^2$H–temperature relation that is used for initialising $\delta^2$H in vapour in our simulations. Section B.3 explains why and how fractionation during evaporation from the ocean is switched off. Section B.4 shows the evolution of the idealised cyclone over time. Section B.5 compares the $\delta^2$H values in surface precipitation for the simulations with and without below cloud fractionation. Section B.6 comments on the variation of the $\delta^2$H structures in the vertical. Finally, Section B.7 gives a more detailed explanation on the causes for nonlinearities of $\delta^2$H (where the sum of the three separate simulations differs from the reference).
B.1 Observed isotope trends in previous studies

Table B.1 gives an overview of the isotope trends that have been found in previous studies of cold front passages together with explanations suggested by the respective authors. The explanations are grouped into four categories (see also Section 1.2.2):

1) Arrival of new air masses.
2) Formation of clouds at different heights.
3) Progressive depletion during rainout.
4) Changes in below cloud interactions.

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Table B.1: Observed/simulated isotope trends in cold frontal precipitation (top) and water vapour (bottom) from different studies, their corresponding figure or table in the article, and processes suggested by the authors as possible explanations: (1) arrival of new air masses, (2) formation of clouds at different heights, (3) progressive depletion during rainout, (4) below cloud interactions. Blue tickmarks indicate processes attributed to the descending trend, red to the V-shaped trend, black to both.
B.2 Temperature dependence of the initial $\delta^2$H

We define the vertical and horizontal structure of $\delta^2$H in the initial conditions to depend linearly on temperature, based on an empirical, linear regression function. The values for the calculation of the regression function are taken from the annual mean of a realistic regional climate simulation with COSMOIso for the year 2011. The domain covers most of Europe, the Mediterranean and part of the Atlantic, as well as the northernmost part of Africa (as in Figure 5.1). It includes levels up to 12 km and temperatures between 220 K and 300 K. In total 849152 data points are used. The resulting $\delta^2$H–temperature relation is $\partial(\delta^2$H)/$\partial T = 4.8^{\circ}/K$ (Figure B.1) and is thus slightly weaker than the temperature effect reported by Dansgaard (1964) ($\partial(\delta^2$H)/$\partial T = 5.6^{\circ}/K$), which was measured in precipitation.

Figure B.1: Correlation of annual mean values of $\delta^2$H in water vapour and temperature from a realistic COSMOiso simulation for the year 2011. $r$ indicates the correlation coefficient, $m$ and $n$ are the slope and the intercept of the regression line, respectively. Colours indicate the height above sea level.
B.3 Switching off fractionation during evaporation from the ocean

The ocean is an almost infinite source of stable water isotopes and can change the $\delta^2$H values in the baroclinic channel through evaporation, especially at low levels. Since the initial $\delta^2$H at the lowest model level is not everywhere in equilibrium with the ocean’s $\delta^2$H = 0‰, this change would be disproportionately large at some locations and different for all simulations. As a consequence it would be difficult to distinguish the contribution of the atmospheric processes (cloud fractionation and transport) from the contribution of ocean evaporation. Therefore we keep the ocean’s effect as small as possible by setting $\delta^2$H in the evaporation flux equal to $\delta^2$H at the lowest model level.

B.4 Evolution of the cyclone

Figure B.2 shows the temporal evolution of the idealised cyclone. It starts as a small perturbation of the sea level pressure field in the western part of the baroclinic channel (Figure B.2 a). After one day the first ice clouds form at the northern edge of what will later be the warm front (Figure B.2 b). These clouds produce precipitation to the north-east of the pressure minimum in the course of days 1 and 2 (Figure B.2 c). On day 3 shallow convection starts in the cold sector (Figure B.2 d). The high ice clouds from the cyclone’s warm conveyor belt appear in the northern edge of the warm sector on day 4 and a rain band extends along the cold front (Figure B.2 e). Later on day 5 secondary cyclones start to develop upstream and downstream of the primary cyclone (Figure B.2 f).

B.5 Effects of below cloud interactions on $\delta^2$H in precipitation

Figure B.3 shows $\delta^2$H in surface precipitation for the simulations with and without below cloud fractionation. The difference between the two simulations indicates where below cloud interactions have the largest impact on $\delta^2$H in precipitation. They lead to a clear enrichment in the south of the domain, where precipitation falls as rain, and to a slight depletion in the north, where precipitation occurs in the form of snow. This is consistent with previous studies (e.g., Field et al., 2010; Pfahl et al., 2012).
B.6 Sensitivity of $\delta^2$H to the selection of the vertical level

Figure B.2: Evolution of the cyclone in the baroclinic channel. Shown are the equivalent potential temperature at the lowest model level (shaded), sea level pressure (lines), and the isosurfaces of cloud water (light blue, 200 mg/kg), cloud ice (dark grey, 10 mg/kg), rain (dark blue, 10 mg/kg) and snow (white, 40 mg/kg).

B.6 Sensitivity of $\delta^2$H to the selection of the vertical level

For the analysis of $\delta^2$H in water vapour (Figure 4.3) we chose the 3.1 km level, since there $\delta^2$H shows a clear signal in all simulations and precipitation consists of both the liquid and solid phase. Selection of a different level would not change the results significantly. Vertical transport and cloud fractionation are slightly stronger at higher levels, while horizontal transport is very similar. Only close to the surface the signals look different, since evaporation from the ocean blurs the effect of the atmospheric processes, and vertical transport is weaker. The same holds for the time series of $\delta^2$H during the cold frontal passage (Figure 4.5). In the lowest 1 km there is almost no effect of fractionation and vertical transport, and no V-shaped trend of $\delta^2$H. At levels higher than $\sim$ 3 km precipitation occurs mainly as snow, and $\delta^2$H decreases (without V-shape) due to transport and the amount effect.
Figure B.3: $\delta^2$H in surface precipitation for (a, b) the simulations with and without below cloud fractionation, and (c) the difference between the two. Note the different colour scale for (c).

B.7 Nonlinearities of $\delta^2$H

Here we discuss the possible causes of nonlinearities (where sum ≠ reference; see Section 4.4.2) in more detail.

1. The nonlinearity of the $\delta$ scale. The same strength of fractionation (in terms of the equilibrium fractionation factor $\alpha_{v/l}$ between vapour and liquid) leads to larger changes of $\delta^2$H if $\delta^2$H is less negative. For example, if $\alpha_{v/l}$ is 0.9 and $\delta^2$H in water vapour is −100‰, then $\delta^2$H in the condensate is 0 under equilibrium conditions. For the same $\alpha_{v/l}$ if $\delta^2$H in water vapour is −300‰, then $\delta^2$H in the condensate is −222‰, and the difference between the condensate and the water vapour is smaller. This effect is even larger for smaller $\alpha_{v/l}$ (stronger fractionation). Hence a higher initial $\delta^2$H potentially leads to stronger depletion of the water vapour and stronger enrichment of condensates, wherever fractionation occurs.

2. Falling rain equilibrates with the surrounding vapour and thereby changes its isotopic composition. More enriched water vapour gives more enriched rain, and vice versa. Apart from the first effect of the $\delta$ scale the difference between rain and vapour does not depend on the absolute background $\delta^2$H, but on its gradient in the vertical column. Rain that is formed from depleted vapour at high levels and falls through more enriched vapour at lower levels will become more enriched than rain that forms and falls in a uniform vertical column. Hence the rain in the simulations with a vertical gradient of $\delta^2$H is potentially more enriched than in the simulations without a vertical gradient.
Appendix C

Seasonal cyclone and front anomalies

Figures C.1–C.4 show the seasonal anomalies of temperature (left), precipitation / rainout (middle), and evaporation (right) of air masses associated with a cyclone compared to air masses not associated with a cyclone from (a) the Eulerian, and (b) the Lagrangian perspective. The Lagrangian anomaly of rainout is given as a ratio, all other variables are given as differences. The Eulerian precipitation and evaporation are 1 hourly accumulated. Stippling indicates areas where $p < 0.01$.

Figures C.5–C.8 show the seasonal anomalies of $\delta^2$H (left) and deuterium excess (right) of air masses associated with a cyclone compared to air masses not associated with a cyclone from (a,b) the Eulerian, and (c) the Lagrangian perspective. The Eulerian $\delta^2$H and deuterium excess values are shown in precipitation (a), and water vapour (b). Stippling indicates areas where $p < 0.01$.

Figures C.9–C.12 and Figures C.13–C.16 show the same as Figures C.1–C.4 and Figures C.5–C.8 but for air masses associated with a front compared to air masses not associated with a front.
C.1 Cyclones

(a) Eulerian

(b) Lagrangian

Figure C.1: Same as Figure 5.33, but for spring (MAM).

(a) Eulerian

(b) Lagrangian

Figure C.2: Same as Figure 5.33, but for summer (JJA).
Figure C.3: Same as Figure 5.33, but for autumn (SON).

Figure C.4: Same as Figure 5.33, but for winter (DJF).
Figure C.5: Same as Figure 5.34, but for spring (MAM).

Figure C.6: Same as Figure 5.34, but for summer (JJA).
Figure C.7: Same as Figure 5.34, but for autumn (SON).

Figure C.8: Same as Figure 5.34, but for winter (DJF).
C.2 Fronts

(a) Eulerian

![Image of Eulerian maps showing temperature, precipitation, and evaporation anomalies for spring (MAM).]

(b) Lagrangian

![Image of Lagrangian maps showing temperature, rainout, and evaporation anomalies for spring (MAM).]

Figure C.9: Same as Figure 5.35, but for spring (MAM).

(a) Eulerian

![Image of Eulerian maps showing temperature, precipitation, and evaporation anomalies for summer (JJA).]

(b) Lagrangian

![Image of Lagrangian maps showing temperature, rainout, and evaporation anomalies for summer (JJA).]

Figure C.10: Same as Figure 5.35, but for summer (JJA).
Figure C.11: Same as Figure 5.35, but for autumn (SON).

Figure C.12: Same as Figure 5.35, but for winter (DJF).
**Figure C.13:** Same as Figure 5.36, but for spring (MAM).

**Figure C.14:** Same as Figure 5.36, but for summer (JJA).
Figure C.15: Same as Figure 5.36, but for autumn (SON).

Figure C.16: Same as Figure 5.36, but for winter (DJF).
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