

Spatial and temporal variability of snow isotopic composition on Mt. Zugspitze, Bavarian Alps, Germany

Kerstin Hürkamp^{1*}, Nadine Zentner^{1,2}, Anne Reckerth¹, Stefan Weishaupt³, Karl-Friedrich Wetzel³, Jochen Tschiersch¹, Christine Stumpp^{2,4}

¹ Helmholtz Zentrum München, German Research Center for Environmental Health, Institute of Radiation Protection, Ingolstädter Landstraße 1, 85764 Neuherberg, Germany.

² Helmholtz Zentrum München, German Research Center for Environmental Health, Institute of Groundwater Ecology, Ingolstädter Landstraße 1, 85764 Neuherberg, Germany.

³ University of Augsburg, Institute of Geography, Alter Postweg 118, 86159 Augsburg, Germany.

⁴ University of Natural Resources and Life Sciences, Institute of Hydraulics and Rural Water Management, Muthgasse 18, 1190 Vienna, Austria.

* Corresponding author. Tel.: +49 89 3187 2582. Fax: +49 89 3187 3363. E-mail: kerstin.huerkamp@helmholtz-muenchen.de

Abstract: High amounts of precipitation are temporarily stored in high-alpine snow covers and play an important role for the hydrological balance. Stable isotopes of hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) in water samples have been proven to be useful for tracing transport processes in snow and meltwater since their isotopic ratio alters due to fractionation. In 18 snow profiles of two snowfall seasons, the temporal and spatial variation of isotopic composition was analysed on Mt. Zugspitze. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ranged between -26.7‰ to -9.3‰ and -193.4‰ to -62.5‰ in 2014/2015 and between -26.5‰ to -10.5‰ and -205.0‰ to -68.0‰ in 2015/2016, respectively. Depth-integrated samples of entire 10 cm layers and point measurements in the same layers showed comparable isotopic compositions. Isotopic composition of the snowpack at the same sampling time in spatially distributed snow profiles was isotopically more similar than that analysed at the same place at different times. Melting and refreezing were clearly identified as processes causing isotope fractionation in surficial, initial base or refrozen snow layers. For the future, a higher sampling frequency with detailed isotopic composition measurements during melt periods are recommended to improve the understanding of mass transport associated with snowmelt.

Keywords: Stable isotopes of oxygen and hydrogen in water; Snow profile; Snowmelt runoff; Isotope fractionation.

INTRODUCTION

In high alpine environments, meltwater from catchments with temporary snow cover and glaciers plays an important role for the hydrological balance and peak discharge in spring during melt periods (Holko et al., 2011). Runoff patterns are clearly influenced by the temporal storage of precipitation in the form of snow and ice (Viviroli et al., 2003, 2011). Snow has a high efficiency for washout of contaminants from the atmosphere. They can be accumulated in the snow cover and released into surface waters in relatively short time periods after snowmelt initiation in spring and affect water quality (e.g., Johannessen and Henriksen, 1978; Kępski et al., 2016). For balancing the water and contaminant budgets, knowledge of the snow processes involving accumulation, metamorphism and snowmelt is necessary. Measurements of the stable isotopes of hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) in water samples (in the following referred to as “stable isotopes”) have been proven to be useful for tracing flow paths and transport processes in snow since their isotopic ratio alters due to fractionation processes (e.g., Ala-aho et al., 2017; Clark and Fritz, 1997; Juras et al., 2016). In addition, variations in the stable isotope content in precipitation, which are mainly influenced by rainout processes and temperatures, are reflected in fresh snow covers (Stichler, 1987). Generally, higher summer, autumn and spring temperatures correspond to higher isotope ratios in precipitation, whereas lower winter temperatures result in lower isotope ratios. Therefore, snow and snowmelt are depleted in heavy isotopes. This can be traced in catchments for identifying the impact of glacier or snow meltwater in the hydrological cycle

(Stichler and Schotterer, 2000). Furthermore, precipitation formed at higher altitudes is usually more depleted in heavy isotopes than at lower altitudes (Dansgaard, 1964). This was also observed on Mt. Zugspitze (Lauber and Goldscheider, 2014). A linear $\delta^{18}\text{O}$ decrease of $-0.2\text{‰}/100\text{ m}$ was found for the Alps (Siegenthaler and Oeschger, 1980). This altitude effect is the result of the temperature effect combined with higher humidity at high altitude as low temperatures and high humidity lead to pronounced fractionation (Clark and Fritz, 1997). An altitude effect has been also observed in solid precipitation in several studies, e.g. by Moser and Stichler (1970) or Dietermann and Weiler (2013). These studies showed that the effect is less pronounced in solid than in liquid precipitation. However, an altitude effect has only been found in fresh snow and snow samples from the beginning of the snow period as the snow undergoes further fractionation processes with time. In altered snow, isotopic signatures change due to condensation, evaporation, sublimation, snow metamorphism, snowmelt processes and water vapour diffusion caused by temperature variations (e.g., Sokratov and Golubev, 2009; Unnikrishna et al., 2002; van der Wel et al., 2011). Evaporation and sublimation processes due to solar irradiance of the upper layers of the snowpack result in enrichment of the heavy isotopes in the snow (Moser and Stichler, 1974; Stichler et al., 2001). Water vapour diffusion between pore spaces and snowmelt can lead to isotopic smoothing and homogenisation (Arnason et al., 1972; Martinec et al., 1977). In melting snow the light isotopes will prevail in the initial runoff fractions (Stichler and Schotterer, 2000). With time meltwater becomes enriched in heavy isotopes as a consequence of isotopic exchange between liquid

water and ice as the meltwater percolates down in the snowpack (Taylor et al., 2001). Also external influences like wind, rain-on-snow events (Juras et al., 2016, 2017) or ground heat fluxes lead to isotope fractionation processes (Stichler, 1987; Stichler and Schotterer, 2000).

Most of the previous studies analysing isotope ratios in snow focus on the investigation of specific processes during melting (Martinec et al., 1977; Moser and Stichler, 1974; Stichler et al., 2001; Taylor et al., 2001; Unnikrishna et al., 2002) or compare the isotopic composition in the snow depth profiles with isotopes in precipitation at the end of the winter period (Arnason et al., 1972; Holko, 1995; Moser and Stichler, 1974). However, it remains to be tested whether conditions affecting the isotopic composition within the snowpack at the plot scale can be generalised to larger areas of snow accumulation in local alpine areas. Further, the temporal variation of isotopes in the snowpack during the accumulation period could give more detailed information about the potential local effects like redistribution of snow, interim snowmelt or homogenisation processes. This study aims (a) to characterise the temporal variation of stable isotopes in snow profiles at the same location, (b) to identify the spatial variability of stable isotopes in snow, and (c) to give implications that can be drawn from the isotope fractionation for mass transport processes in the snowpack. These objectives were achieved by investigating snow pits at Zugspitzplatt, Mt. Zugspitze (2962 m a.s.l.), Bavarian Alps, Germany.

MATERIAL AND METHODS

Study Site

Investigations were carried out at the so-called Zugspitzplatt, a karstic plateau of 1500–2800 m of altitude (mean 2229 m a.s.l.) composed of 600–800 m thick bedded limestones (“Wettersteinkalk”, Ladin) with a slightly undulating relief. It is surrounded by several summits and inclined to the east (Fig. 1). The underlying layer consists of 300–400 m of marly claystone (“Partnach-Schichten”), which serves as an aquiclude (Miller, 1962). Zugspitzplatt shows forms of glacial erosion and accumulation from the Younger Dryas and of the Little Ice Age (1550–1850). Large areas covered by frost debris are also existent (Hüttl, 1999). Abundant soil covers do not exist. At the eastern margin of the 11.4 km² catchment, surface water infiltrating and draining through the karst aquifer discharges at a geological fault in the Partnach spring (1440 m a.s.l., Wetzel, 2004). The Partnach gauge (see Fig. 1), where discharge is continuously recorded, is situated 200 m downstream and 75 m of altitude beneath the spring. 3.5% (0.4 km²) of the catchment is permanently covered with snow and ice (Nördlicher and Südlicher Schneeferner glacier, data from 2009 (Rappl et al., 2010)). Average annual temperature on the highest summit (Mt. Zugspitze, 2962 m a.s.l.) is –4.8°C. Between 1998–2011, in the lower parts of the catchment (<1900 m), temperatures only exceeded 0°C in 54 days, in the upper parts (>2500 m) in 6 days during the snow accumulation period (Weber et al., 2016). The average annual precipitation on Mt. Zugspitze is 2071 mm (1981–2010); mainly snow at 58% of all days and 90% of the precipitation days per year (DWD, 2017). The variability of snow cover duration is between 33 and 338 days (1998–2011, Weber et al., 2016). The region is strongly wind exposed and experiences intensive solar radiation. Wind characteristics differ between Zugspitzplatt and Mt. Zugspitze summit, where fresh precipitation samples were taken. Wind velocities at the summit are approximately twice as high as at the plateau. Wind directions are limited at the plateau, because it is surrounded by wind-sheltering mountain ridges to the north, south and west.

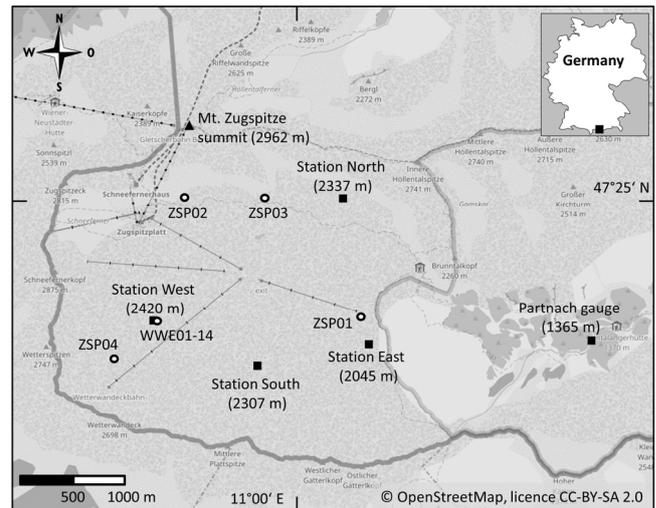


Fig. 1. Spatial distribution of snow profiles at Zugspitzplatt (“WWE” and “ZSP”, bullets) as well as location of the meteorological stations (squares).

Nevertheless, small-scaled turbulences lead to different local wind fields.

Snow and fresh precipitation sampling

For the investigation of the temporal variation of stable isotope contents in the snow, snow pits were dug every two weeks (generally on the 1st and 15th day of a month between December 2014 and May 2015 and again from January to May 2016) at Station West (2420 m a.s.l.) on Zugspitzplatt (Fig. 1). An area of approximately 20 m x 20 m surrounding an installed meteorological station was fenced for it to protect the undisturbed snow cover from ski tourism. The profile excavations started in one corner at the beginning of the snow accumulation season each year and followed a grid of 5 m x 5 m to the adjacent profile each 15 days. The order of the profiles was the same in both seasons, but the day of the first sampling was different, related to a minimum snow depth of 50 cm. For the investigation of the spatial variability of isotopes in snow, four profiles (labelled with “ZSP01–04”, Fig. 1) were additionally excavated on March 14th to 16th, 2016 at different remote locations on Zugspitzplatt. The choice of sites was limited to only a few areas that are not affected by extreme wind induced snow drift, steep slope gradients or ski tourism. All sampling locations are situated on solid bedrock or coarse block debris without soil cover.

The time period for the sampling of ZSP01–04 was kept short (3 days) in order to minimise strongly variable climatic influences. It enables a better comparison of all profiles related to their location rather than to external impact. The Zugspitzplatt is inclined to the east and receives sun during the mornings. The northern parts which are exposed to the south are illuminated in the afternoons. The locations in the south are most often shaded, since they are shielded by the southern mountain ridge. Wind patterns vary due to local roughness of the relief and rapidly changing wind directions of gusts. East-west directions dominate, even though the turbulence is high (Risius et al., 2015). The selected locations are representing sites with different slopes, solar and wind exposure and are expected to give a representative distribution of stable isotopes in the entire Zugspitzplatt catchment.

Eighteen snow profiles were excavated up to the depth of the solid bedrock (Table 1). Snow characteristics were described in detail according to Fierz et al. (2009). Snow layers were distin-

Table 1. Snow profile parameters and statistics of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values.

| profile ID | sampling date | altitude (m a.s.l.) | location coordinates | | total depth ¹⁾ (cm) | sampling interval | number of samples | SWE ²⁾ (mm) | $\delta^{18}\text{O}$ min (‰) | $\delta^{18}\text{O}$ max (‰) | $\delta^2\text{H}$ min (‰) | $\delta^2\text{H}$ max (‰) | SWE ²⁾ -weighted mean $\delta^{18}\text{O}$ (‰) | SWE ²⁾ -weighted mean $\delta^2\text{H}$ (‰) |
|------------|---------------|---------------------|----------------------|---------------|--------------------------------|-------------------|-------------------|------------------------|-------------------------------|-------------------------------|----------------------------|----------------------------|--|---|
| | | | latitude | longitude | | | | | | | | | | |
| WWE01 | 2014-12-15 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 90 | layer-wise | 6 | 357.9 | -21.6 | -13.5 | -160.1 | -92.2 | -16.3 | -115.0 |
| WWE02 | 2014-12-31 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 196 | layer-wise | 10 | 494.0 | -26.7 | -13.3 | -193.4 | -92.5 | -18.2 | -129.8 |
| WWE03 | 2015-02-01 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 225 | layer-wise | 8 | 803.8 | -23.5 | -13.4 | -175.7 | -94.8 | -20.4 | -150.5 |
| WWE04 | 2015-03-01 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 221 | layer-wise | 6 | 797.8 | -17.8 | -14.2 | -131.0 | -102.8 | -16.4 | -118.9 |
| WWE05 | 2015-03-29 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 245 | layer-wise | 12 | 989.1 | -21.1 | -11.0 | -156.6 | -77.9 | -16.5 | -119.7 |
| WWE06 | 2015-04-14 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 319 | layer-wise | 10 | 1364.9 | -16.6 | -10.4 | -121.1 | -68.8 | -14.9 | -106.8 |
| WWE07 | 2015-04-30 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 276 | layer-wise | 12 | 1395.7 | -18.1 | -10.2 | -132.9 | -65.3 | -16.1 | -116.1 |
| WWE08 | 2015-05-13 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 223 | layer-wise | 23 | 1203.3 | -20.0 | -9.3 | -152.3 | -62.5 | -15.1 | -108.3 |
| WWE09 | 2016-01-15 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 198 | layer-wise | 12 | 570.1 | -19.1 | -13.7 | -146.2 | -103.6 | -16.9 | -124.2 |
| WWE10 | 2016-02-15 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 280 | 10 | 28 | 1047.9 | -24.9 | -12.7 | -192.9 | -89.7 | -17.6 | -127.6 |
| WWE11 | 2016-03-14 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 260 ⁴⁾ | 10 | 26 | 1041.5 | -26.5 | -12.1 | -205.0 | -86.5 | -18.3 | -134.0 |
| WWE12 | 2016-04-01 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 410 | 30 | 14 | 1843.2 ³⁾ | -22.3 | -13.6 | -173.5 | -101.8 | -17.3 | -130.7 |
| WWE13 | 2016-04-16 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 228 | 30 | 10 | 1073.3 | -18.9 | -13.5 | -140.5 | -93.5 | -17.0 | -125.3 |
| WWE14 | 2016-05-03 | 2420 | 47°24'22.75"N | 10°59'00.39"E | 270 | 10 | 29 | 1223.6 | -20.4 | -10.5 | -153.9 | -68.0 | -16.4 | -121.3 |
| ZSP01 | 2016-03-15 | 2053 | 47°24'22.05"N | 11°00'22.07"E | 290 | 20 | 15 | 1107.4 ³⁾ | -24.2 | -12.8 | -188.4 | -94.3 | SWE ²⁾ not determined | |
| ZSP02 | 2016-03-15 | 2528 | 47°24'56.10"N | 10°59'06.34"E | 220 | 20 | 11 | 807.7 ³⁾ | -21.7 | -11.9 | -159.5 | -89.5 | SWE ²⁾ not determined | |
| ZSP03 | 2016-03-16 | 2446 | 47°24'55.10"N | 10°59'42.67"E | 230 | 20 | 12 | 867.7 ³⁾ | -26.0 | -12.5 | -201.9 | -93.8 | SWE ²⁾ not determined | |
| ZSP04 | 2016-03-16 | 2509 | 47°24'09.49"N | 10°58'38.72"E | 170 | 20 | 9 | 628.0 ³⁾ | -22.8 | -14.0 | -179.8 | -106.2 | SWE ²⁾ not determined | |

¹⁾ snow and profile depth above solid bedrock (no soil cover)

²⁾ SWE = snow water equivalent

³⁾ SWE taken from a contemporaneous snow profile dug by the Bavarian Avalanche Warning Service at WWE-location

⁴⁾ depth of bedrock was not reached, total depth of profile is 395 cm

guished considering differences in snow texture, grain size, roundness, hardness and water content of the snowpack. Snow densities were determined *in situ* in 30 cm depth intervals (independent of layers) with a metal tube of known volume. A spring scale was used to measure the sample weight. Snow water equivalents (SWE) were calculated from the *in situ* snow densities for each snow layer (Table 1). SWE was used to quantify the amount of precipitation fallen between two sampling dates. It is also used for the correlation of the isotopic composition in the snow profiles compared to that of fresh precipitation, determined in samples of Mt. Zugspitze summit. Additional data useful in the interpretation of the results were provided by the snow pack analyser sensor (Sommer and Fiel, 2009) which measured the liquid water content of the snowpack 10 cm above the bedrock. Meteorological information was delivered by four additional meteorological stations (Station North, South, East, West, Fig. 1) that cover the entire Zugspitzplatt.

Bulk snow samples for the determination of stable isotopes were generally taken as depth-integrated samples over the total depth of the recorded snow layers in 2015. The thickness varied between a few millimetres for ice layers and maximum 123 cm. In 2016, the procedure was changed and uniform sampling depth intervals of 10 cm layers were applied without considering the snow layering. In the profiles of April 2016 (WWE12 and -13) snow of 30 cm layers was merged. Samples were taken by scratching the snow from the profile walls with 100 ml plastic vials, which were tightly sealed for storage. Icy layers were dissected from the surrounding snow and broken into small pieces with a knife to put them into the vials.

The isotopic composition of the snow profiles was compared to that in fresh precipitation of the same time period. The German Meteorological Service (Deutscher Wetterdienst, DWD) collected daily samples of freshly fallen precipitation from the ground at Zugspitze summit (2962 m a.s.l.) and merged them to biweekly bulk samples (Table 2). For the amounts of precipitation, SWE was continuously recorded at Station West using a snow balance (Smith et al., 2017). Even though this method is more prone to SWE losses/gains due to wind drift or intermediate snowmelt, assessing the solid precipitation amount at wind

exposed sites is even more difficult and imprecise when using traditional precipitation gauges (Lundberg et al., 2016b), that are also available at Zugspitze summit and at Station West. Unless there is mass loss of snow due to meltwater runoff at the snow base, as it is proven for the study site during the winter months (see section “Snow cover and meltwater runoff development 2014–2016 at Zugspitzplatt”), it is feasible to compare SWE of precipitation and accumulated snowpack.

Sample pre-treatment and measurement of stable isotopes

Snow and ice samples were melted under closed conditions within the sampling vials before analysis. Precipitation and melted snow samples were analysed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ratios using laser spectroscopy (Picarro L2120-i). A two point calibration with laboratory reference material calibrated against VSMOW-SLAP (Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation) scale was used. Each sample was measured up to nine times. Precision of the instrument (1σ) was better than 0.15‰ and 0.6‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively. Results of stable isotope compositions in precipitation and snow are presented as the ratio of isotopes (R_{sample}), given in the delta notation as δ -value (‰), which is the relative deviation of the sample from a standard (R_{standard}):

$$\delta(\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \cdot 1000$$

All samples were referenced to the VSMOW-SLAP scale. More details about measurement techniques and principles of isotope hydrology are given by IAEA (1983), Wassenaar et al. (2014) and Leibundgut et al. (2009).

For the comparison of the stable isotopic composition between precipitation samples taken at Zugspitze summit (2962 m a.s.l.) and snow samples of Zugspitzplatt (2420 m a.s.l.) an altitude correction factor was introduced accounting for the 542 m elevation difference. From comparison of measured stable isotopes in mainly solid precipitation sampled at the summit with samples at Hoher Peißenberg (988 m a.s.l.) between 2014–

2015 an altitude correction factor of $-0.12\text{‰}/100\text{ m}$ for $\delta^{18}\text{O}$ and of $-0.78\text{‰}/100\text{ m}$ for $\delta^2\text{H}$ was determined (not part of this study, personal communication C. Stumpp). Accordingly, corrections of $+0.65\text{‰}$ and $+4.23\text{‰}$ were applied to the measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ ratios for fresh precipitation at Mt. Zugspitze summit, respectively, to compare them with the isotopic composition of snow at Zugspitzplatt (Table 2).

Craig (1961) observed that the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation that has not been evaporated are linearly related by $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$, known as the "Global Meteoric Water Line" (GMWL). The slope and intercept of a "Local Meteoric Water Line" (LMWL), which is the line derived from precipitation collected from a single site, can be significantly different from the GMWL. In this study, LMWL were calculated from the precipitation samples applying an ordinary least squares regression according to Hughes and Crawford (2012) with the equation $\delta^2\text{H} = a \delta^{18}\text{O} - b$. With the same method also dual isotope regression lines were calculated for the snow samples using mean snow water equivalent (SWE)-weighted values of all isotope ratios. Parameters for the two lines were compared and discussed. Deuterium (d)-excess was calculated as $d = \delta^2\text{H} - 8 \delta^{18}\text{O}$, and used in identification of water evaporation and comparison of isotopic composition of precipitation at Mt.

Zugspitze and other German stations. Evaporated water typically plots below the meteoric water line along lines that intersect the MWL at the location of the original unevaporated composition of the water.

RESULTS

Snow cover and meltwater runoff development 2014–2016 at Zugspitzplatt

The measured snow parameters at Station West ("Wetterwanddeck") since 2012 revealed that there was almost no mass loss of snow during the winter months from November to April, as shown for the winters 2014/2015 and 2015/2016 in Fig. 2. This means, the altitude and recent meteorological conditions at this site induced a continuous accumulation of snow and prevented meltwater runoff at the snow base during the winters. However, surface melting and snowpack compaction certainly occurred. Fig. 2 shows the daily means of snow height, snow water equivalent (SWE), density and liquid water content at the snow base at Station West in the snowfall seasons 2014/2015 and 2015/2016. The corresponding water discharge, recorded at the Partnach gauge (1365 m a.s.l.), initiated in late April in both years.

Table 2. Precipitation amount and altitude-corrected isotopic composition of precipitation measured at Mt. Zugspitze summit (2962 m a.s.l.).

| sampling date | | amount (mm) | $\delta^{18}\text{O}_{\text{corr.}}$ (‰) | $\delta^2\text{H}_{\text{corr.}}$ (‰) | d-excess (‰) | accumulated weighted mean | |
|---------------|------------|-------------|--|---------------------------------------|--------------|--|---------------------------------------|
| from | to | | | | | $\delta^{18}\text{O}_{\text{corr.}}$ (‰) | $\delta^2\text{H}_{\text{corr.}}$ (‰) |
| 2014-10-17 | 2014-10-31 | 159.1 | -11.0 | -69.1 | 18.9 | -11.0 | -69.1 |
| 2014-11-01 | 2014-11-16 | 40.4 | -18.0 | -132.1 | 11.8 | -12.4 | -81.8 |
| 2014-11-17 | 2014-11-30 | 23.1 | -14.9 | -112.6 | 6.8 | -12.7 | -85.0 |
| 2014-12-01 | 2014-12-16 | 15.6 | -13.4 | -92.4 | 14.8 | -12.7 | -85.5 |
| 2014-12-17 | 2014-12-31 | 190.9 | -22.7 | -174.1 | 7.6 | -17.2 | -124.9 |
| 2015-01-01 | 2015-01-16 | 108.5 | -12.0 | -87.4 | 8.8 | -16.1 | -117.4 |
| 2015-01-16 | 2015-01-31 | 140.2 | -19.9 | -148.3 | 11.2 | -16.9 | -123.7 |
| 2015-02-01 | 2015-02-16 | 69.3 | -16.0 | -112.9 | 15.4 | -16.8 | -122.7 |
| 2015-02-16 | 2015-02-28 | 22.9 | -19.6 | -145.7 | 11.3 | -16.9 | -123.4 |
| 2015-03-01 | 2015-03-16 | 158.9 | -12.3 | -89.4 | 9.3 | -16.1 | -117.6 |
| 2015-03-16 | 2015-03-31 | 79.5 | -12.2 | -83.6 | 14.0 | -15.8 | -114.9 |
| 2015-04-01 | 2015-04-16 | 180.0 | -12.5 | -91.1 | 9.3 | -15.3 | -111.3 |
| 2015-04-16 | 2015-04-30 | 17.8 | -13.1 | -95.7 | 9.5 | -15.3 | -111.1 |
| 2015-05-01 | 2015-05-16 | 40.8 | -15.9 | -118.4 | 8.4 | -15.3 | -111.3 |
| 2015-11-17 | 2015-11-30 | 182.1 | -20.4 | -155.1 | 8.1 | -20.4 | -155.1 |
| 2015-12-01 | 2015-12-16 | 43.3 | -14.2 | -101.3 | 12.0 | -19.2 | -144.8 |
| 2015-12-17 | 2015-12-31 | 24.8 | -12.6 | -87.2 | 13.7 | -18.5 | -139.1 |
| 2016-01-01 | 2016-01-15 | 215.3 | -17.7 | -130.1 | 11.6 | -18.2 | -134.9 |
| 2016-01-16 | 2016-01-31 | 141.8 | -17.4 | -122.7 | 16.6 | -18.0 | -132.1 |
| 2016-02-01 | 2016-02-15 | 200.2 | -14.3 | -104.2 | 10.2 | -17.1 | -125.2 |
| 2016-02-16 | 2016-02-29 | 129.4 | -19.0 | -146.9 | 5.4 | -17.3 | -128.2 |
| 2016-03-01 | 2016-03-16 | 55.6 | -17.0 | -129.6 | 6.1 | -17.3 | -128.3 |
| 2016-03-17 | 2016-03-31 | 35.1 | -12.0 | -96.2 | 0.2 | -17.1 | -127.2 |
| 2016-04-01 | 2016-04-16 | 38.5 | -10.2 | -71.4 | 10.3 | -16.9 | -125.1 |
| 2016-04-17 | 2016-04-30 | 109.3 | -13.3 | -100.3 | 6.2 | -16.6 | -122.8 |
| 2016-05-01 | 2016-05-16 | 184.4 | -11.0 | -80.2 | 7.8 | -15.8 | -117.1 |
| 2016-05-17 | 2016-05-31 | 199.0 | -8.3 | -55.9 | 10.2 | -14.8 | -109.2 |

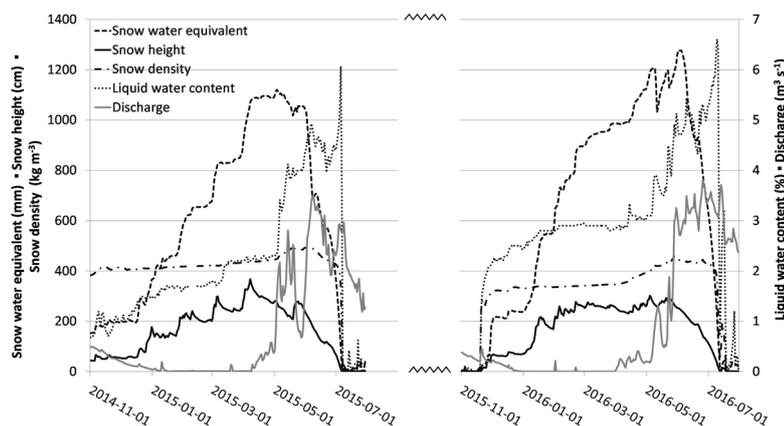


Fig. 2. Records of daily mean snow parameters for the total snow cover at Station West, Zugspitzplatt and water discharge at Partnach spring for the seasons 2014/2015 and 2015/2016. Liquid water contents and displayed densities were measured by the snow pack analyser sensor in the snow 10 cm above the bedrock.

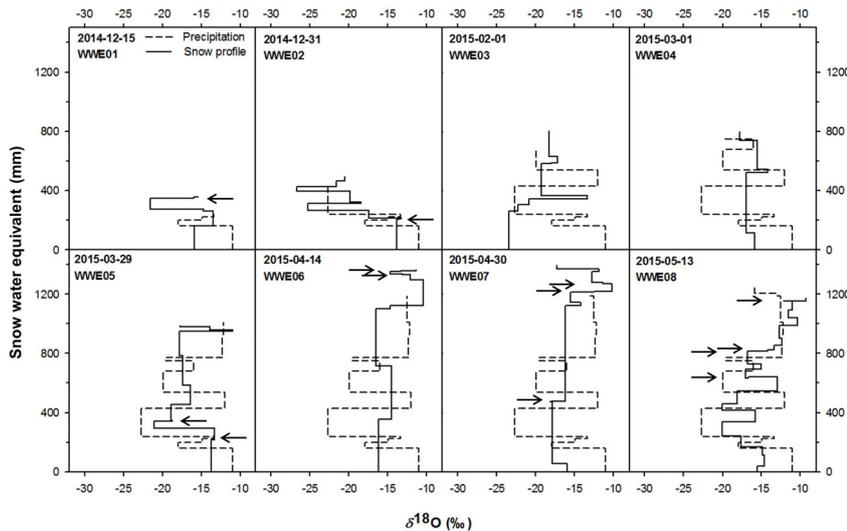


Fig. 3. Temporal variability of altitude corrected $\delta^{18}\text{O}$ contents in precipitation and in the snow samples of the winter season 2014/2015 at Station West, Zugspitzplatt. The arrows mark determined ice layers.

The accumulation of snow during the winter months was represented in the continuously increasing amount of water in the snow (SWE). In contrast, the snow height sometimes decreased due to snow compaction and partial melt which coincided with an increase of snow density. Meltwater runoff during these periods can be precluded, because no mass loss was observed on the snow balance. In 2015, the beginning of meltwater saturation at the snow base was on March 11th, accompanied with increased liquid water contents and snow density. On May 3rd, snowmelt runoff at the bottom of the snowpack began. The strongest melt period was in early June after an intermediate period of frost and snowfall between May 19th–27th. In 2016, water saturation at the snow base began on April 12th, and again on May 6th with increasing density and liquid water contents. Runoff at the snow base started on May 9th. A next peak of meltwater runoff occurred on May 21st and complemented in continuous runoff from the first week of June on.

Temporal variability of stable isotope composition of snow at Zugspitzplatt

The total snow water equivalent (SWE) of the winter season 2014/2015 in the profiles at Station West continuously increased until end of April and afterwards decreased due to the beginning of snowmelt runoff (Figs. 2 and 3). Snowmelt was accompanied by mean air temperatures of 0.2–9.1°C, recorded at Station West between May 1st and 13th, 2015. SWE in the snow profiles and corresponding amounts of fresh precipitation did not always match, likely due to the difference in altitude and wind patterns between the sampling locations. $\delta^{18}\text{O}$ isotope ratios (and $\delta^3\text{H}$ in brackets) ranged between –26.7‰ in December 2014 (–205.0‰ in March 2016) and –9.3‰ (–62.5‰) in May 2015. The depth distribution of stable isotopes, given in $\delta^{18}\text{O}$ values in Fig. 3, is heterogeneous, variable over time, and does not follow the expected distribution. In recent snow an isotopic distribution with lower $\delta^{18}\text{O}$ values during the winter months and higher ones in spring and autumn would be expected, similar to the seasonal input signal in precipitation. However, in the first two profiles (WWE01 and WWE02) of the snow accumulation period 2014/2015, isotopes in the snow samples were most similar to the precipitation values neglecting differences in SWE.

Layers of freshly fallen snow with low densities, as observed during the profile descriptions, were represented by low $\delta^{18}\text{O}$ values, as for example in the surficial layers of WWE04 and

WWE07 (Fig. 3). Distinct minima in the uppermost half of the December 2014 profiles (WWE01 and –02) corresponded to cold periods under changing air mass directions. Low $\delta^{18}\text{O}$ values (<–21.6‰ and <–25‰) after several icy days (<–10°C) also between December 26th and 30th, 2014 (see WWE02). From April on, isotopes measured in the surficial snow layers always had higher values compared to fresh precipitation samples (WWE06–08).

The total SWE in the profiles of the winter 2015/2016 at Station West (Fig. 4) continuously increased until the end of March. Afterwards it massively decreased by more than 600 mm due to the beginning of snowmelt with recorded mean air temperatures about 4°C between May 8th and 11th, 2016. A comparably large decrease in SWE was not observed on the snow balance (Fig. 2). Isotopic composition of snow and precipitation showed different isotope ratios over time. $\delta^{18}\text{O}$ ranged between –26.5‰ (March 2016) and –10.5‰ (May 2016). Surprisingly, in snow profiles from April on (particularly WWE13, Fig. 4) the isotopic composition of snow was in accordance to the isotope ratios measured in precipitation, except for an enrichment of isotope ratios at the snow base. In contrast to the previous year, no pronounced enrichment compared to precipitation was found at the top of the snow profile at the end of the accumulation period. Still, the highest isotope values (–10.5‰) were measured in the top layer of the last snow profile (WWE14).

For both investigated years depth distributions of stable isotopes in the snow were strongly variable over time. Comparing consecutive sampling events, isotopic composition was different in the newly dug profiles, except for the period between profiles WWE10 and WWE11, where the isotopic distribution in the snow nearly stayed constant over four weeks in February/March 2016. It should be kept in mind that different sampling depth intervals and changes in snow density have to be considered in the interpretation. Larger sampling depth intervals lead to an apparent homogenisation (e.g. WWE07).

Spatial variability of stable isotopes in snow profiles at Zugspitzplatt

Air temperatures during the sampling of ZSP01–04 within 3 days in March 2016 were between –15–0°C. Two short precipitation showers (<1.3 mm) occurred on the 14th evening and the 15th within two hours after noon. Otherwise it was sunny. Snow depth was about 260 cm at Station West. Measured snow water equivalent was 950 mm. Wind intensities were below 5 m s^{–1},

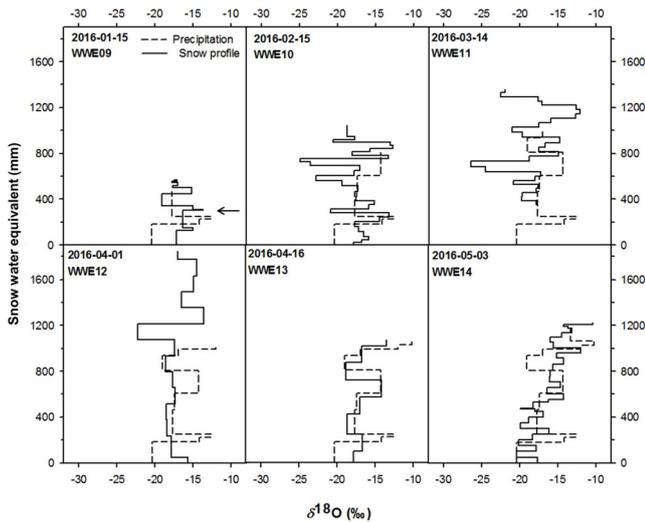


Fig. 4. Temporal variability of altitude corrected $\delta^{18}\text{O}$ contents in precipitation and in the snow samples of the winter season 2015/2016 at Station West, Zugspitzplatt. The arrow marks one determined ice layer. Later in the year, the thickness of the investigated ice layers was too small to accurately separate them as individual samples.

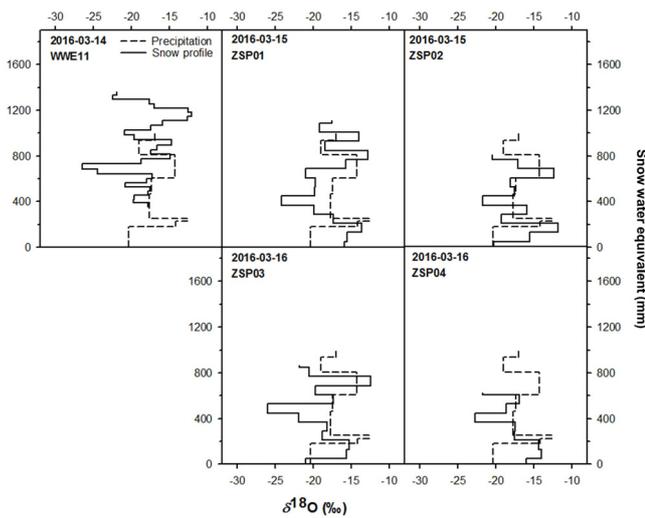


Fig. 5. Spatial variability of altitude corrected $\delta^{18}\text{O}$ contents in precipitation and in snow samples collected at different locations at the Zugspitzplatt (see Fig. 1).

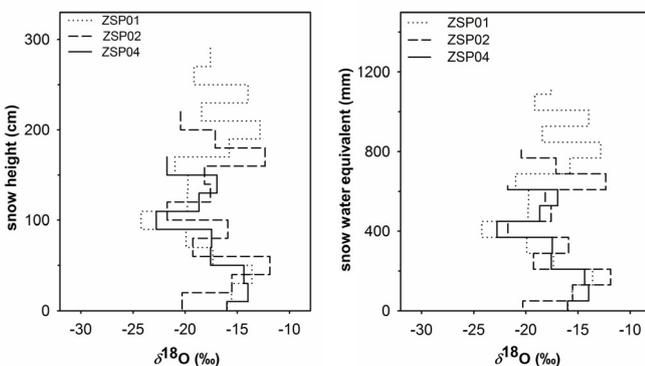


Fig. 6. Spatial variability of $\delta^{18}\text{O}$ contents of selected snow profiles of March 15th/16th, 2016 at remote locations on Zugspitzplatt. Despite different expositions, the patterns of stable isotope stratification in the profiles are similar.

except for a windy period with northeasterly gusts up to 10 m s^{-1} during the snowfall event on March 15th. Snow water equivalents (SWE) in the fresh precipitation samples differed from those measured by the snow balance indicating loss (ZSP02-04) or gain (WWE11 and ZSP01) in the local profiles compared to precipitation. Despite different locations of the snow pits and different external influences, a similar trend of the depth gradient of the isotopic composition in the snow profiles ZSP01-04, dug in the same week, could be observed.

All profiles taken in March 2016 fall into the range of isotope values that would have been expected from isotope measurements in precipitation (Fig. 5). In the deeper parts of the profiles (up to 600 mm SWE) the depth distribution of the $\delta^{18}\text{O}$ ratios in snow followed the same trend (Fig. 6) towards higher values in the base layers compared to fresh precipitation (Fig. 5), and lower ones in the layers at about 400 mm SWE. Similarity of spatially different profiles taken at the same time was higher compared to similarity of the same location sampled at different times.

DISCUSSION

Variability of snow water equivalents at Zugspitzplatt

Deviations of maximum 365 mm in ZSP04 between the determined snow water equivalents (SWE) in the snow profiles and precipitation were found (Fig. 5, Tables 1 and 2). This concerns profiles taken at the same time but at different locations (up to 2.5 km distance) emphasizing the importance of local conditions on the snow accumulation (e.g. relief, wind, Lundberg et al., 2016a). Deviations can be explained by the different sampling locations at Zugspitzplatt in different altitudes, expositions and wind regimes. Consequently, different amounts of SWE between the profiles must be attributed to the undulating relief with small wind-protected troughs in which snow accumulated and was preserved, whereas in wind-exposed positions mainly fresh and dry snow was removed. Huge variability of average SWE (1998–2011) at Zugspitzplatt with three times higher SWE in the west than at its eastern margin was also found by Weber et al. (2016). These variations were linked to annual as well as long-term variations in meteorological/climatological conditions.

In addition to these differences at the larger scale, the difference in SWE between the WWE profiles at Station West and the adjacent snow balance was even larger in one case (max. 857 mm in WWE12). In general, lower SWE were determined by the snow balance. This leads to the assumption that besides measurement uncertainties of the device considerable loss by wind drift or snowmelt on the snow balance occurred since the onset of the snow accumulation period. Consequently, the influence of snow redistribution is important not only on the large scale but also on the local plot scales.

Comparison of isotope values in snow depth profiles and precipitation

Comparing the isotopic composition of the snow profiles, the different depth intervals used in this study have to be considered. Larger sampling depth intervals automatically resulted in an apparent decrease in variability compared to smaller intervals. The same applied to precipitation sampling representing average values for biweekly integrative samples. Consequently, differences in isotope values of individual precipitation events might still have been visible in snow profiles with high resolution depth intervals, but could not be distinguished in the bulk precipitation sample. Still, the overall weighted isotope composition should be similar.

Applying a sampling depth interval of 10 cm as performed in 2016, the difference between taking depth-integrated mixed samples of the entire layer or selective point snow samples (horizontal penetration in the middle of each snow layer to fill the vials) in an additional profile close to Station West on February 24th, 2016 is shown in Fig. 7. Obviously, the results of both methods do not differ significantly, but will most likely be higher when using more coarse sampling resolution.

In an $^{18}\text{O}/^2\text{H}$ diagram (Fig. 8), all samples from the snow profiles plot close to the Local Meteoric Water Line (LMWL) with a mean of $\delta^2\text{H} = 8.08 \delta^{18}\text{O} + 11.46$ for both winter seasons 2014/2015 and 2015/2016. The intercept and slope, as well as the d-excess (10.2‰), are higher compared to other stations in Germany (Stumpp et al., 2014), but still are in the range of other high alpine stations (Rank and Papesch, 2005). The slopes of the snow sample regression lines for both years (8.11 and 7.83) are lower compared to the precipitation LMWL indicating that evaporation or sublimation effects caused isotope fractionation. The data points that lie below the precipitation LMWL belong to samples that underwent sublimation and evaporation processes at the snow surface during prolonged periods of sunshine, resulting in enhanced snow metamorphism. Still, isotope fractionation effects should be of minor relevance in high alpine regions during periods of high humidity in winter (Stichler et al., 2001). Such periods frequently occur due to cloud coverage of Mt. Zugspitze, but can become more relevant during foehn events with extremely low relative humidity.

With some exceptions (e.g. WWE13 and ZSP01), the poor conformity of isotopic composition in snow and precipitation seems -not solely- to be attributed to processes within the snow, but also to snow redistribution by the wind. The importance of wind drift on snow transport and redistribution at Zugspitzplatt has been shown earlier (Bernhardt et al., 2012). Seasonal evolution of volume weighted means of $\delta^{18}\text{O}$ of snow (weighted by SWE) and accumulated precipitation (weighted by precipitation amount) as well as the calculated d-excess are shown in Fig. 9. The weighted means of isotopic composition of snow and precipitation are also given in Tables 1 and 2. Particularly for the d-excess, deviations between snow and precipitation can be the result of uncertainties due to the altitude correction of the precipitation data. The $\delta^{18}\text{O}$ means in precipitation and snow profiles converge over time. Some values of single snow profiles (e.g., February 1st, 2015) clearly deviate from the precipitation data, possibly due to higher ice contents or snow drift at specific times of the year. Nevertheless, throughout the winter season the mean isotope signature of winter precipitation is well preserved in the mean of the last snow profiles. It suggests that local deviations measured at individual times are averaged out. The overall conformity shown in Fig. 9 lets us to believe that the comparison of the isotopic composition of precipitation and snow is reasonable after altitude correction.

Temporal variability of stable isotopes in snow at Zugspitzplatt

Looking at the temporal variability of stable isotopes in the snow profiles, processes within the snowpack and processes caused by redistribution can be distinguished in more detail. At the snow base lower isotope ratios were found in snow compared to precipitation in winter 2014/2015 and *vice versa* in winter 2015/2016. This may be due to unknown deposition or melting processes before or after the snow accumulation period, indicated by fluctuating amounts of snow water equivalents (SWE). Melting at the snow base due to ground heat flux from

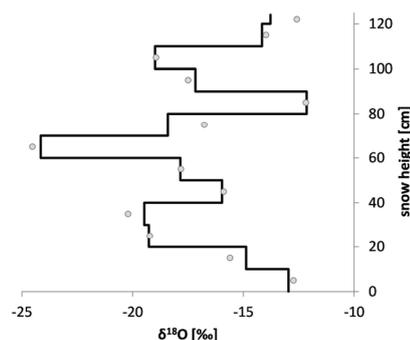


Fig. 7. $\delta^{18}\text{O}$ values in an additional snow profile close to Station West: Differences between the sampling methods of bulk samples (line) and point source samples (bullets).

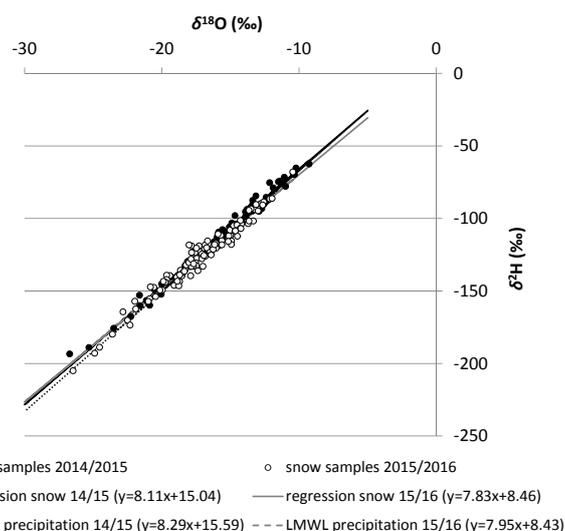


Fig. 8. Dual isotope plot for all snow samples of the seasons 2014/2015 and 2015/2016 with linear regression lines and the Local Meteoric Water Lines (LMWL) generated from biweekly fresh precipitation samples of the same period.

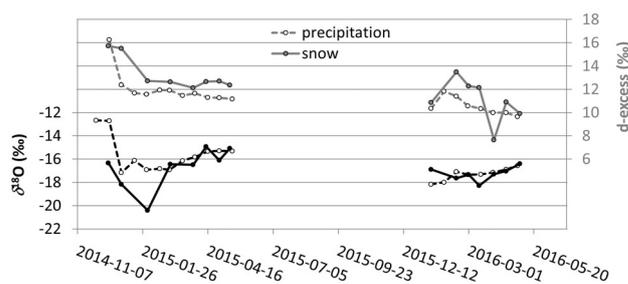


Fig. 9. Accumulated altitude corrected weighted $\delta^{18}\text{O}$ contents in biweekly precipitation samples and SWE-weighted means of $\delta^{18}\text{O}$ in the snow profiles (black lines) and the d-excess (grey lines) for the same samples in the seasons 2014/2015 and 2015/2016.

the still warm bedrock in November each year could have resulted in the removal of light isotopes from the initial snowpack and thus to an enrichment of heavy isotope ratios in the remaining snowpack (compared to precipitation). In contrast, when melting was induced by solar radiation at the top of the snowpack, the light isotopes of the melting snow could have refrozen within deeper snow layers or accumulated at the base above frozen ground. Here, they do not necessarily have left the snowpack, as observed in autumn 2014. The determined high density of the lowermost layer of WWE03 (514 kg m^{-3}) and

extremely low $\delta^{18}\text{O}$ can be explained in this context by a refrozen highly water-saturated base layer.

Melting processes were not only of importance at the beginning and at the end of the snow accumulation. They also caused changes of the snow and the isotopic composition throughout the winter period. Icy layers formed when snow was exposed to the atmosphere during pronounced sunny periods. Partial snowmelt began, before the layer was covered by subsequent snowfall again. Melt and subsequent nocturnal refreezing or following frost periods decrease condensation temperatures and lead to grain coarsening and ice formation (Nakawo et al., 1993). If icy layers were present in the profiles, they were recorded and separately analysed for isotopes, too. They are marked by arrows in Fig. 3 and 4 and usually show slight deviations of isotope ratios to higher values, but do not significantly differ from the bulk snow. As described earlier, the formation of ice due to melting or refreezing of meltwater can be distinguished by the isotopic composition because percolating meltwater preferentially removes light isotopes (Taylor et al., 2001; Zhou et al., 2008). If isotope values of the icy layers were higher compared to the surroundings, it is more likely that melting was initiated at the top of the snowpack and these layers were the remainder of the top layer (see e.g. the thin layers in a depth of 319 mm SWE in WWE02 or in 959 mm SWE in WWE05, Fig. 3). In contrast, if isotope values of the icy layers were lower compared to the surroundings, it is more likely that melted water re-froze within the profile (see e.g. in a depth at 1154 mm SWE in WWE08 (Fig. 3) or at 478 mm SWE in WWE14 (Fig. 4)).

Melting processes, but also vapour diffusion within snow profiles result in a homogenisation of the snow isotopic composition in the snowpack (Stichler, 1987), which was also observed in the present study. This is evidenced by a reduction in amplitudes of the $\delta^{18}\text{O}$ ratios in the course of the year, e.g. when comparing WWE10 and WWE14 having similar depth intervals. In addition, both profiles of the end of the accumulation period (WWE08, WWE014) have a distinct isotopic distribution with high values at the top decreasing to lower values at the base. This was caused by the percolation of isotopically light meltwater through the profile and exchanging isotopes with the ambient snow. In such cases, the stable water isotopes can be used as tracers for mass transport in a snow profile, since it is proven that contaminants deposited as single layers on top of a snowpack will be released within the first portions of meltwater (Bales et al., 1989; Hürkamp et al., 2017; Juras et al., 2016, 2017). The beginning of meltwater percolation in the snowpack was also recorded by an increase of liquid water contents detected by the snow pack analyser and the loss of mass after onset of runoff, determined by the snow balance (Fig. 2) during the same time interval in beginning May 2015 and 2016. The transport within the snowpack was associated with the percolation of liquid water and first initiates after the snow became ripe, this means isothermal at 0°C . In future, it would be worth to also study in more detail the isotopic composition during melting. By comparing snow depth profiles with the isotopic composition of meltwater over time not only under controlled conditions (Moser and Stichler, 1970) or in models (Ala-aho et al., 2017) but also in the field, we can improve the understanding of isotope transport within the snowpack. Also local influences on isotope fractionation, such as rain-on-snow-events (Juras et al., 2016, 2017; Würzer et al., 2017) could be better traced. Here, weighable snow lysimeters would help to regularly collect snowmelt (Rücker et al., this issue).

What has been mentioned earlier, and what was most unexpected, was the poor similarity of the isotopic composition in snow between the consecutive snow profiles (Fig. 3 and 4). The

only case where the isotopic distribution pattern in snow nearly stayed constant over four weeks in February/March 2016 is apparent in the profiles WWE10 and WWE11 (Fig. 4). During this period the mean air temperatures were about 3°C lower (-7.5°C) and relative humidity 12% higher than in the following period between the excavations of WWE11 and WWE12. It indicates better snow conservation and less metamorphism processes. In contrast, high similarity of isotope depth profiles over time were found from daily, weekly or biweekly sampling of snowpack in the Western Tatra Mountains, Slovakia (Holko, 1995), Hokkaido, Japan (Hashimoto et al., 2002; Zhou et al., 2008) or in the Sierra Nevada, USA (Unnikrishna et al. 2002). Even in a previous study at the Zugspitzplatt, sampling of snow profiles between January and July 1972 showed rather stable snow isotope depth profiles over time (Moser and Stichler, 1974). It remains unknown whether differing weather conditions, the shorter sampling time intervals or the fact that they always took their samples from the same snow pit could be the reason for the better recovery of the temporal isotopic variation in the snow 1972. In the present study, new snow pits were dug to avoid isotope fractionation in the old depth profiles. In future, it needs to be tested whether shorter time intervals with similar sampling strategies would give more information about the causes of lacking temporal similarity.

Spatial variability of stable isotopes in snow at Zugspitzplatt

In contrast to the WWE profiles, the isotopic composition of all ZSP profiles was comparable; despite their rather large distances (up to 2.5 km) to each other. Even similarity between the depth gradients of snow and precipitation isotope composition existed; compressed or stretched for some ranges of snow water equivalents (SWE) though. Best agreement of isotope ratios of snow and fresh precipitation showed the profile ZSP01 (Fig. 5). It was the easternmost profile which was located at the lowest altitude (~ 2000 m a.s.l.) at the entrance to the Reintal valley. It is likely that snow metamorphism due to insolation and the alteration of the isotopic snow composition were less pronounced in this area due to cold air streams in the valley, frequent cloud coverage and fog. Therefore, initial isotopic signals remained in the snow.

ZSP02 and -03 profiles contained one and ZSP01 two layers with higher isotope values ($>-15\text{‰}$) in a range between 600–700 mm SWE (Fig. 5). When looking at the precipitation data for dating these layers, they corresponded to periods of sunshine and ambient temperatures above 0°C between January 25th and February 3rd and on February 21st/22nd, 2016. During these days snow surface temperatures rose to isothermal 0°C , inducing high evaporation and sublimation rates as well as initiation of snowmelt. It is possible that the melted water infiltrated and was represented by the light isotopes in the layer at about 400 mm SWE. Certainly, ZSP01 and ZSP04 were influenced by gains and losses of mass when looking at the SWE. Strong wind periods that were detected on February 1st, 10th and 20th–22th, 2016 at all four meteorological stations (wind intensities up to 18 m s^{-1} and gusts up to 30 m s^{-1}) can explain the low SWE compared to precipitation in profile ZSP04 and the gains at other locations (WWE11 and ZSP01).

Holko et al. (2013) found a high spatial variability in the isotopic composition of the snow cover during a snow-poor winter 2011 in northern Slovakia. For thin snow covers in Canadian Prairies, the same was investigated by Pavlovskii et al. (2017). According to Dietermann and Weiler (2013), the spatiotemporal isotopic distribution in a snowpack is strongly dependent

on the exposition, altitude and day in the year. Distinct spatial variability was also found for north and south-facing slopes in the Austrian Oetztal Alps (Schmieder et al., 2016), especially during the early melt season. In our study it remains difficult to distinguish the role of exposition or altitude (e.g. by comparing weighted isotopic averages), because the water balance is strongly influenced by the redistribution of snow within the study area. Stichler and Schotterer (2000) emphasised that particularly in summit regions of the Alps, redistribution and partially removal/accumulation of snow are the main processes influencing the isotopic composition of the snowpack or even glaciers. All studies point out the need of isotope measurements in each stage of hydrologic pathways for their use as tracers for transport processes concerning snowmelt runoff.

CONCLUSIONS

Eighteen snow pits in the hydrologic catchment of the Partnach creek, draining the Zugspitzplatt, were dug and sampled for the determination of temporal and spatial variability of the stable water isotopes in the snow. The temporal variability of the isotopic composition in 14 snow profiles of the seasons 2014/2015 and 2015/2016 at Station West at a small scale was extremely pronounced despite close proximity of the profiles, indicating complex processes happening in the snowpack. This can be either due to redistribution of snow between the biweekly sampling campaigns or due to processes causing changes of isotope ratios within the snow profile. Both are likely because changes and non-uniformity of snow water equivalents indicated snow gains and losses. In addition, recorded strong wind intensities and low temperatures support the argument of enhanced wind drift. Spatial variability of isotopic composition of snow layer samples at the same time but at different locations was much smaller than the above mentioned temporal. Melting and refreezing were clearly identified processes that caused isotope fractionation. Surficial, initial base or refrozen layers could be distinguished by the isotopic content. Isotope ratios were heavier compared to the surrounding layers due to the release of isotopically light meltwater or were lighter due to meltwater enrichment, respectively.

In future it would be necessary to measure with higher temporal frequency, because the similarity of isotopic composition between the biweekly sampling dates was low. It is recommended to stay with higher resolution depth profiles (e.g. 10 cm sampling depth intervals, ideally at concurrent consideration of the snow layering) to also get information about potential homogenisation throughout the winter period caused by vapour diffusion or melting. Due to large spatial differences and the dissimilarity between isotopes in snow and in precipitation, it remains to be studied how this will effect larger catchment modelling, where values from precipitation are available. In the future, also weighable snow lysimeters would help to get better information about changes of the snow water equivalent over time and at the same time the melting water could be collected to measure changes in isotopes and any other potential contaminants released due to the snowmelt.

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