applied sciences

MDPI

Article

Factors Influencing Changes of the Initial Stable Water Isotopes Composition in the Seasonal Snowpack of the South of Western Siberia, Russia

Tatyana Papina *, Alla Eirikh and Tatiana Noskova

Institute for Water and Environmental Problems SB RAS, 656038 Barnaul, Russia; allnik608@gmail.com (A.E.); ntv.lady@yandex.ru (T.N.)
* Correspondence: tanya.papina@mail.ru; Tel.: +7-385-2666444

Abstract: Stable water isotopes in snowpack and snowfalls are widely used for understanding hydrological processes occurring in the seasonally snow-covered territories. The present study examines the main factors influencing changes of the initial stable water isotopes composition in the seasonal snow cover of the south of Western Siberia. Studies of the isotopic composition of snow precipitation and snow cover, as well as experiments with them, were carried out during two cold seasons of 2019–2021, and laser spectroscopy PICARRO L2130-i (WS-CRDS) was used for the determination of water isotope composition ($\delta^{18}O$ and δD). The main changes in the isotopic composition of the snow cover layers in the studied region are associated with the existence of a vertical temperature gradient between the layers and with the penetration of soil moisture into the bottom layers in the absence of soil freezing. During the winter period, the sublimation from the top layer of snow is observed only at the moments of a sharp increase in the daily air temperature. At the end of winter, the contrast between day and night air temperatures determines the direction of the shift in the isotopic composition of the top layer of snow relative to the initial snow precipitation.

Keywords: stable water isotopes; atmospheric precipitation; snowpack

check for updates

Citation: Papina, T.; Eirikh, A.; Noskova, T. Factors Influencing Changes of the Initial Stable Water Isotopes Composition in the Seasonal Snowpack of the South of Western Siberia, Russia. *Appl. Sci.* **2022**, *12*, 625. https://doi.org/10.3390/app12020625

Academic Editor: Marco Petitta

Received: 9 December 2021
Accepted: 7 January 2022
Published: 10 January 2022

1. Introduction

Data on the stable isotope compositions of oxygen and hydrogen in precipitation and snowpack is actively used to obtain important information about climatic, hydrological, and ecological changes in the environment [1–14], including the assessment of the trans-boundary transfer of atmospheric moisture falling on the studied area as precipitation, and the identification of the sources of this moisture [15–24]. In contrast to snowfalls, seasonal snow cover of middle and polar latitudes can give integral seasonal (for the winter period) characteristics of the moisture's isotopic composition entering the studied area [24–26]. At the same time, the sampling of snowpack during the maximum snow accumulation period is simpler to perform in relation to the sampling of atmospheric precipitation and allows you to cover a large area with the necessary sampling network. Unfortunately, it is not correct to directly use the isotopic composition data of the seasonal snow cover for hydrological, climatic, and ecological purposes because many researchers note that during the winter period various processes leading to changes in the initial isotopic composition of snow can occur in the layers of snowpack [27–48]. All this must be taken into account when snowpack samples are used to assess the seasonal moisture supply and further its redistribution among the components of the water runoff in the catchment area after snow melting.

During the winter period, the main changes in the isotopic composition ($\delta^{18}O$ and δD) of water in the layers of the snowpack are associated with the penetration and condensation of soil moisture in the snow layer closest to the snow-soil interface [27,34,38,40], movement and condensation of moisture (vapor and water) inside the snowpack due to the existence of a vertical temperature and pressure gradients [33,38], partial thawing of snow layers [38–40], as well as vapor exchange between the upper layer of snow and the atmosphere [38–40]. In addition, a significant effect on the change in the isotope composition of the snowpack can be exerted via canopy for forest areas [8,41–43] and for steppe areas due to wind redistribution of snow previously accumulated on the ground [44–46]. All of these processes have different effects on the vertical redistribution of the initial isotopic composition of atmospheric moisture deposited on the underlying surface, and their combined influence can manifest itself in different ways depending on regional weather conditions. Therefore, studying regional peculiarities and factors influencing changes in the snow's initial stable water isotopes composition in the snowpack is an important task with a wide practical application.

For the south of Western Siberia (this territory has a stable seasonal snow cover from mid-November to mid-March), the data of the layer-by-layer analysis of the snowpack can be successfully used to study the features of the spatio-temporal distribution of atmospheric moisture deposited during the winter period. In this regard, the purpose of our work was to identify the main factors and assess their contribution to the change in the initial water isotopic composition ($\delta^{18}O$ and δD) of snowfalls during their storage in seasonal snow cover (until the beginning of the stage of active snow melting) in the south of Western Siberia.

2. Materials and Methods

2.1. Study Area

Altai Territory is located in the south of Western Siberia (Figure 1a) and covers an area of about 168,000 km^2 with a varied relief, including plains (steppe and forest-steppe zones), foothills, and mountains. The region is characterized by a continental climate due to frequent changes in air masses coming from the Atlantic, Arctic, and Central Asia, which determine a large contrast in weather conditions [47,48]. The long-term average annual temperatures range in the Altai Territory is from 1.18 to 3.76 °C [49]. In the summer months, maximum temperatures reach 42 °C. At the same time, rather low temperatures are formed in winter with an absolute minimum down to −52 °C [50]. During the cold period of the year (from October to March), the prevailing wind directions are southern and southwestern [51]. Precipitation in the Altai Territory is not uniform. On the flat part of the territory, the amount of precipitation varies from 240–250 mm in dry-steppe regions to 550–570 mm in forest-steppe regions and increases from 650 to 900 mm in the foothills from west to east [52]. Seasonal snow cover is established in the second decade of November and is destroyed in the first decade of April. The height of the snowpack in the Altai Territory averages 40–60 cm; in the western regions, it decreases to 20–30 cm [48]. The contribution of snow melting to the water runoff of the large Ob River, which originates in the Altai Territory and flows into the Kara Sea, is about 70–80% [53].

In this work, we studied the snowpack and winter precipitation falling on the flat territory of the region, namely, within the catchment area of the Ob River from the city of Biysk to the city of Kamen-na-Obi (Figure 1b). According to the seasonal snow cover classification system [54], the snow cover of the studied area can belong to mixed of two phenomenological classes—the prairie and taiga. The studied area is characterized by a slight gradual decrease in atmospheric precipitation from the south-east to the north-west [55]. The largest city and capital of the Altai Territory, Barnaul, is located in the central part of the studied area. The average annual precipitation for Barnaul is 433 mm, of which ~40% falls in the form of snow [56].

2.2. Sampling

During two cold periods from November to mid-March (winter 2019–2020 and 2020–2021), snowfalls and snow cover samples were recovered to study their water isotopic (δD and $\delta^{18}O$) composition. Sampling was carried out in the catchment area of the Ob River from Biysk city to Kamen-na-Obi city (Figure 1b), while the main work and experiments were carried out in the center part of this area—in and around Barnaul city (Figure 1c). The sampling scheme was as follows:

(1) Samples of snow event-based precipitation during the cold period were collected immediately after their fallout on experimental site III, located on the roof of the building of the Institute for Water and Environmental Problems of the Siberian Branch of the Russian Academy of Sciences (IWEP SB RAS) at the height of 25 m from the earth's surface (Figure 1c). Snowfalls were collected in internal removable high-density polyethylene bags attached inside the barrel, equipped with blowing protection (Supplementary, Figure S1a). A total of 97 event-based snowfalls samples were collected during two cold periods.

(2) The bulk snowpack samples were taken during the period of maximum snow accumulation (at the beginning of March) at the sites of the network (Figure 1b). All sites were located in a field on a flat territory free from trees and bushes. Sampling was performed using the envelope method (10 × 10 m). The composite sample consisted of 5 snowpits collected with a plastic pipe (4.5 cm inner diameter). In March 2020, the bottom layers of snowpack samples (thickness ~5–7 cm) were taken in addition to the bulk ones. In total, 111 snow samples were taken and analyzed.

(3) The following experiments were carried out on three experimental sites (Figure 1c, sites I, II, III) in 2019–2021:

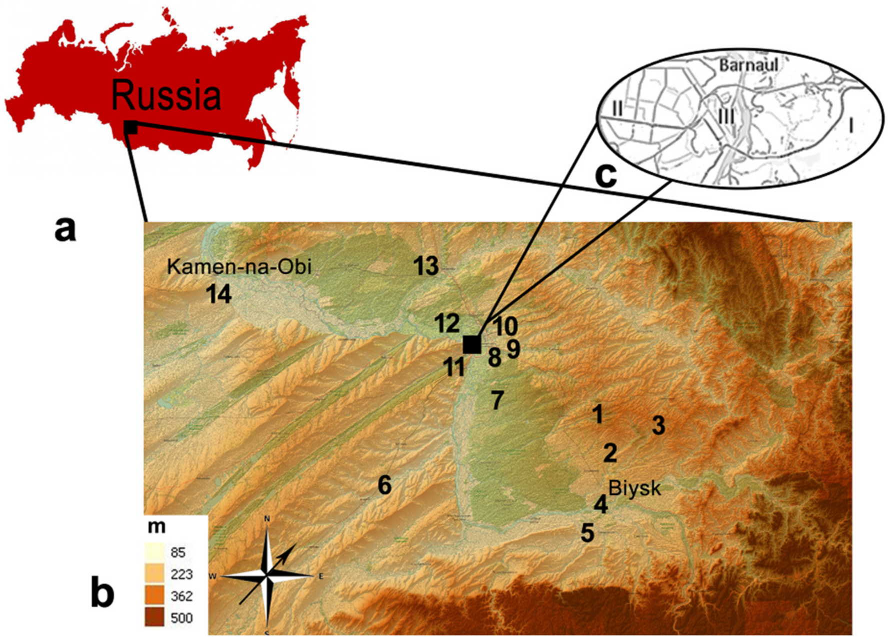


Figure 1. (**a**) Location of the studied area; (**b**) snowpack sampling network. The sampling points are the numbers 1–14; (**c**) location sites for conducting experiments (I, II) and atmospheric precipitation sampling (III).

Experiment No. 1. At the beginning of winter 2019–2020, the 1.5 m high plastic barrel was installed on the roof of the IWEP SB RAS building (site III) in addition to sampling the individual snowfalls. In this barrel, after each heavy snowfall, a layer of fallen snow was separated from subsequent precipitation with a plastic disk. The 11 layers of snow obtained in this way were removed at the end of the winter (Supplementary, Figure S1b) and analyzed separately.

Experiment No. 2. In the winter of 2020–2021, two barrels equipped with wind protection devices were installed on the ground of each of the two sites (Figure 1c, sites I, II). One barrel was intended to sample integral snow precipitation, the second one for a separate sampling of snow layers (similar to experiment No. 1). The barrels' contents were removed for isotopic analysis at the end of winter. Moreover, we sampled two snowpack pits (bulk and layer-by-layer) on the earth's surface near the experimental barrels at the end of winter. Layer-by-layer sampling was carried out with a step as equal as possible to the layers of snow in the corresponding second barrel. For this, we selected nine horizontal layers in each pit (equal to the number of layers in each barrel) and determined their density. Then, we took samples of the pit layers, the height of which in water equivalents was equal to the corresponding layers in the barrel.

After collection, samples of snow (precipitation and snowpack) were placed in clean tight-closing plastic bags and stored frozen until analysis.

2.3. Analytical Methods

All hydrogen and oxygen isotope ratios of precipitation are denoted as δ^2H (or δD) and $\delta^{18}O$, defined by

$$^2H \text{ (or } \delta D) = \left(\frac{(^2H/^1H)_{sample}}{(^2H/^1H)_{V\text{-}SMOW}} - 1 \right) \cdot 1000‰ \quad (1)$$

$$\delta^{18}O = \left(\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{V\text{-}SMOW}} - 1 \right) \cdot 1000‰ \quad (2)$$

where V-SMOW refers to the Vienna Standard Mean Ocean Water

The stable isotope ($\delta^{18}O$, δD) analysis of snow samples was carried out at the Chemical Analytical Center of IWEP SB RAS. Directly before instrumental analysis, snow samples were placed into the closed specially prepared plastic containers [25,34] and melted at room temperature. Then, 10 mL of melted snow water was filtered through a membrane filter with a pore diameter of 0.45 μm using sterile Minisart® NML Plus syringe and syringe nozzles to determine the isotopic (δD and $\delta^{18}O$) composition. Five parallel samples were taken from the filtrate and analyzed by laser absorption IR spectrometry on a PICARRO L2130-i (WS-CRDS) instrument. The measurement accuracy of δD and $\delta^{18}O$ (1σ, n = 5) was ±0.4‰ and ±0.1‰, respectively. The secondary parameter d-excess proposed by W. Dansgaard [57] was calculated as:

$$d - excess = \delta D - 8 \cdot \delta^{18}O \quad (3)$$

Using the error propagation method [58] and starting from errors of $\delta^{18}O$ and δD, the calculated accuracy for d-excess was estimated as ±0.8‰.

Precipitation-weighted mean values of stable isotope compositions (δD, $\delta^{18}O$, and d-excess) in precipitation for the winter period were calculated by the formula:

$$Cvwm = \frac{\sum(Cj \cdot Qj)}{Q} \quad (4)$$

where Cvwm is the seasonally precipitation-weighted mean values, ‰; Cj is the value of δD, $\delta^{18}O$ or d-excess in the j-th precipitation sample, ‰; Qj is the amount of the j-th precipitation sample, mm weq.; Q is the total precipitation amount for the winter period, mm weq.

Similarly, using Formula (4), the depth-weighted mean values of δD, $\delta^{18}O$, and d-excess for a snow cover of the study area were calculated, where Cj is the value of δD, $\delta^{18}O$ or d_{exc} in the snowpack of the j-th sampling point; Qj is the height of the snowpack at the j-th point, mm weq.; Q is the sum of the snowpack's depths at all points, mm weq.

3. Results

3.1. Isotopic Composition of Water in the Initial Event-Based Snow Precipitation

The water isotopic composition of the snow precipitation during the cold period 2019–2020 (from November to mid-March) in the studied area (Barnaul) varied from −30.3‰ to −12.0‰ for $\delta^{18}O$ and from −235.4‰ to −90.7‰ for δD, in the cold period of 2020–2021 the spreading of the isotopic composition values was more significant and varied from −35.6‰ to −11.6‰ for $\delta^{18}O$ and from −277.3‰ to −79.8‰ for δD. The precipitation-weighted mean values were −19.2 and −21.5‰ for $\delta^{18}O$ and −147.4 and −166.6‰ for δD for the cold periods of 2019–2020 and 2020–2021, respectively (Table 1). The precipitation-weighted mean value of deuterium excess (d-excess) was 5.9‰ for the winter of 2019–2020 and 5.7‰ for the winter of 2020–2021, which indicates some depletion of snow precipitation by deuterium atoms (δD) relative to $\delta^{18}O$. Local meteoric water line (LMWL) calculated by the equation $\delta D = 8.1 \times \delta^{18}O + 8.1$ ($R^2 = 0.98$) for the O-D isotopic data of the event-based snowfalls samples in the cold period 2019–2020 (Supplementary, Figure S2a) indicates a slight excess of the slope relative to the global meteoric water line (GMWL), calculated by the equation $\delta D = 8 \times \delta^{18}O + 10$ [16]. For the cold period 2020–2021, the LMWL for the O-D isotopic data of the event-based snowfalls samples was calculated by the equation: $\delta D = 7.9 \times \delta^{18}O + 3.1$ ($R^2 = 0.98$), where the slope is already slightly lower than the slope value of the GMWL (Supplementary, Figure S2b). The statistical estimates of LMWL for event-based snowfall samples (errors of the estimates for slopes and intercepts) are given in Table S1 in Supplementary Materials.

Table 1. Comparison of the isotopic composition of the bulk snowpack samples with the initial atmospheric precipitation for the winter period 2019–2020 (1) and 2020–2021 (2).

	$\delta^{18}O$, ‰		**δD, ‰**		**D-Excess, ‰**	
	1	**2**	**1**	**2**	**1**	**2**
Snowpack, n = 14 (sampling points 1–14, Figure 1b)						
max	−18.6	−18.7	−144.6	−141.5	6.4	8.4
min	−21.9	−23.2	−170.3	−179.7	2.2	4.2
mean [1]	−20.0	−20.4	−155	−157	4.7	6.4
SDOM [2]	0.6	0.7	4.3	5.6	0.6	0.8
Atmospheric precipitation (n = 47 for 2019–2020; n = 50 for 2020–2021)						
max	−12.0	−11.6	−90.7	−79.8	11.3	17.2
min	−30.3	−35.6	−235.4	−277.3	−6.1	−9.5
mean [3]	−19.2	−21.5	−147.4	−166.6	5.9	5.7
SDOM [2]	0.1	0.1	0.4	0.4	0.8	0.8

[1] depth-weighted mean; [2] SDOM—standard deviation of the mean; [3] precipitation-weighted mean for the same period as the snowpack.

3.2. Water Isotopic Composition of Snowpack

The spread in the values of the water isotopic composition in the snowpack (bulk samples) in the studied area (Figure 1b) during the period of maximum snow accumulation varied in winter 2019–2020 from −21.9‰ to −18.6‰ for $\delta^{18}O$ and from −170.3‰ to −144.6‰ for δD, and in winter 2020–2021 from −23.2‰ to −18.7‰ for $\delta^{18}O$ and from −179.7‰ to −141.5‰ for δD (Table 1). The calculated depth-weighted (mm of weq) mean values of the water isotopic composition of the snow cover were −20.0‰ and −20.4‰ for $\delta^{18}O$ and −155‰ and −157‰ for δD, respectively, for the cold period 2019–2020 and 2020–2021. Figure S2a,b (Supplementary Materials), show the LMWL for snow samples taken at the end of winter 2019–2020 and 2020–2021. Relationship δD-$\delta^{18}O$ in snow cover is calculated by the equation $\delta D = 7.9 \times \delta^{18}O + 2.9$ ($R^2 = 0.98$) for winter 2019–2020 and by the equation $\delta D = 7.7 \times \delta^{18}O + 0.4$ ($R^2 = 0.98$) for winter 2020–2021, which are located below LMWL for the winter precipitation in the corresponding cold period (Figure S2a,b). The statistical estimates of LMWL for snowpack samples (errors of the estimates for slopes and intercepts) are given in Table S1 in Supplementary Materials.

At the end of winter 2019–2020, the snowpack's lower layers (depth hoar) were taken at all sampling sites in addition to the bulk samples. The isotopic composition of water in the bottom layers of snow adjacent to unfrozen soils was noticeably heavier (on average by 4.5‰ for $\delta^{18}O$ and by 33‰ for δD) relative to the corresponding bulk samples (Table 2), while the lower layers of snow on frozen soil differed insignificantly (on average by 0.8‰

for $\delta^{18}O$ and by 9‰ for δD). The LMWLs for the lower layers of snow are presented in Figure S2a separately for those on frozen and non-frozen soil.

Table 2. Comparison of the isotopic composition of the bulk snowpack samples (1) with the bottom layer of the snowpack (2) depending on the soil freezing in winter 2019–2020.

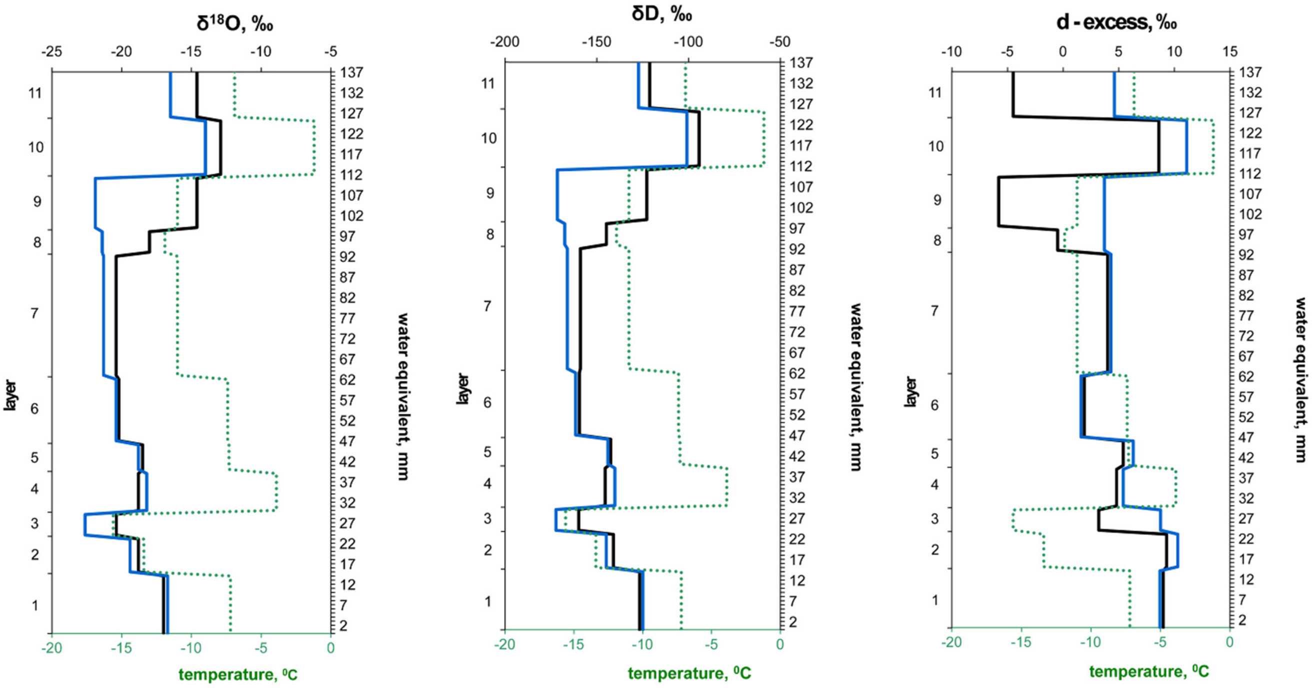
	Depth, mm w. Eq.		**$\delta^{18}O$, ‰**		**δD, ‰**		**D-Excess, ‰**	
	1	**2**	**1**	**2**	**1**	**2**	**1**	**2**
Frozen soil (n = 8): sampling points [1] 2, 4, 5, 6, 7, 9, 10, 13								
max	155	20	−19.1	−17.7	−147.2	−134.6	6.4	9.8
min	78	14	−21.9	−20.8	−170.3	−158.0	2.4	4.4
mean [2]	129	18	−20.3	−19.5	−158	−149	5	7
SDOM [3]			0.6	0.7	4.3	5.9	1.0	1.1
No soil freezing (n = 6): sampling points [1] 1, 3, 8, 11, 12, 14								
max	180	23	−18.6	−14.1	−144.6	−113.0	5.8	3.5
min	134	17	−21.7	−16.6	−168.5	−130.3	3.4	-1.9
mean [2]	162	21	−20.0	−15.5	−155	−122	5	1
SDOM [3]			0.8	0.9	7.0	5.3	0.7	1.6
Atmospheric precipitation (snow n = 47; rain n = 12)								
snow [4]	150	33	−19.2	−17.8	−147.4	−133.5	6	9
rain [5]		48		−10.9		−88.9		−2.1
SDOM [3]			0.1	0.1	0.4	0.4	0.8	0.8

[1] number according to Figure 1b; [2] arithmetic mean for the depth; depth-weighted mean for $\delta^{18}O$, δD, d-excess; [3] SDOM—standard deviation of the mean; [4] precipitation-weighted mean for the same period as the snowpack layers; [5] precipitation-weighted for the last two months before snow cover.

3.3. Layer-by-Layer Analysis of Snowpack, Data of Experiments

Figure 2 shows the change in the isotopic composition of water in the isolated 11 snow layers (from the bottom to the upper), which were taken out of the barrel at the end of winter 2019–2020 (Experiment No 1; site III, Figure 1c). For comparison, the figure shows the precipitation-weighted mean values of water isotopic composition in the event-based snowfalls and the average daily air temperature calculated for the same period as the layers of snow were formed in the barrel. The figure shows that the changes in $\delta^{18}O$ and δD in the layers of snow and in the precipitation-weighted mean value of snowfalls correlate well both with each other and with the change of the average daily temperature. At the same time, significant differences in the isotopic composition between the isolated layers of snow and the initial compositions of snowfalls are observed at the moments of a sharp increase in air temperature, when lighter water isotopes condensed at lower temperatures can sublimate from the layer of snow back into the atmosphere even under the separating plastic disk (along its edges). This situation was observed for layers 3, 8, and 9 (Figure 2). In addition, lower values of deuterium excess in these snow layers relative to the initial snowfalls indicate the existence of isotopic fractionation of snow in them.

The results of experiments to study changes in the isotopic composition of the water in the initial snow precipitation, during their storage in the layers of snow cover in the winter of 2020–2021 (experiment No. 2), are shown in Figure 3. To display all results at once, we used a single scale, where the value of the water equivalent of each layer is the arithmetic mean of the components of the figure since the water equivalents of the identified layers of snow in barrels (experimental sites I and II, Figure 1c) and snow precipitation sampled for a similar period (site III, Figure 1c) differ no more than by 25%.



(**a**) (**b**) (**c**)

Figure 2. Comparison of changes in the isotopic composition ($\delta^{18}O$ (**a**), δD (**b**), d-excess (**c**)) in isolated layers of snow in the barrel (black), according to experiment No. 1 (see Section 2.2), with the precipitation-weighted mean values of the isotopic composition of the event-based snowfalls (blue) and the mean of the daily average air temperature (green dot line) calculated for the same period of winter 2019–2020.

Figure 3 shows that changes in the isotopic composition of water in nine isolated layers of the snowpack sampled at both experimental sites were close to each other and correlated well with the precipitation-weighted mean values of the water isotopic composition in the initial event-based snowfalls and the average daily temperature calculated for the same period (Figure 3a,c). A completely different picture is observed in the snowpack formed directly on the ground, the layers of which were not isolated from each other and were not protected from wind redistribution. The vertical distribution of the isotopic composition in such a snowpack was smoothed—the maximum differences did not exceed 10‰ for $\delta^{18}O$ and 75‰ for δD while for the layers in the barrel, it reached 20‰ for $\delta^{18}O$ and 160‰ for δD. The water isotopic composition in these layers differed from those in the barrel layers, and the calculated precipitation-weighted mean values of the initial event-based snowfalls and did not correlate with the average daily temperature (Figure 3b,d). In 2020–2021, similarly to the 2019–2020 experiment, differences in the isotopic composition between the isolated layers of snow and the initial compositions of snowfalls are observed at the moments of a sharp increase in air temperature (layers 4, 6, and 8). However, since the experimental sites in 2020–2021 were located at a noticeable distance from each other (sites II and III in the city on the high left bank of the Ob River, and site I outside the city on the floodplain section of the right bank), it is quite understandable why for the 8th layer this regularity observed only in urban areas.

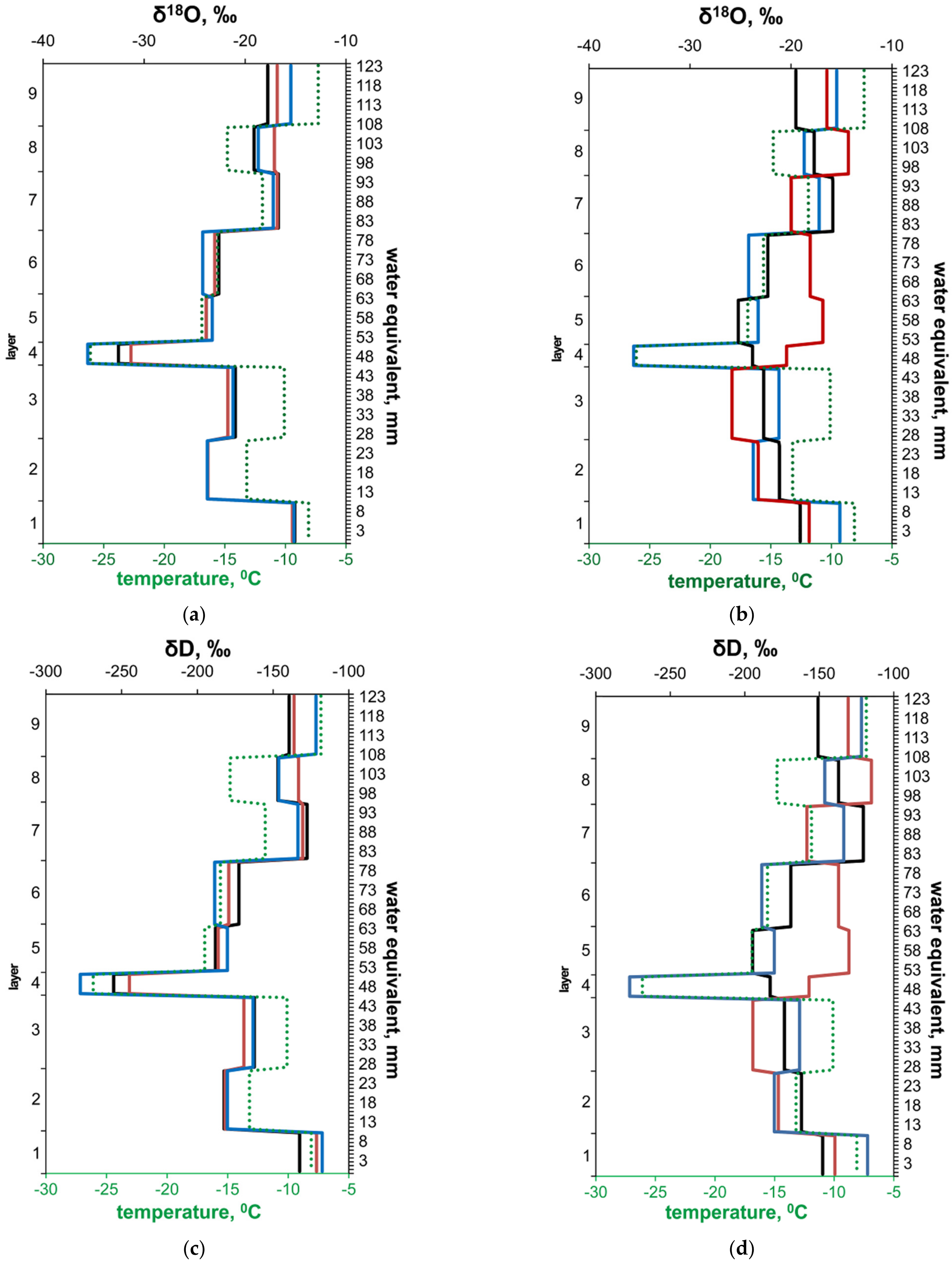


Figure 3. Comparison of changes in the isotopic composition ($\delta^{18}O$ and δD) of snowfalls during their storage in the snowpack layers (experiment No. 2, winter period 2020–2021). Black—layers of snow in experimental site I; red—layers of snow in experimental site II; blue—precipitation-weighted mean of the event-based snowfalls; green dot line—mean of the daily average air temperature ((**a**,**c**)—snowpack in the barrel; (**b**,**d**)—snowpack on the soil).

4. Discussion

Many authors [27,28,33,40,59,60] point to the vertical homogenization of the isotopic variance within the snowpack due to diffusion and dispersion of liquid and vapor molecules of water inside the snow masses. In our case, this is clearly manifested in the smoothing of the vertical change in the isotopic composition of the snowpack formed on the earth's surface, in contrast to the isolated snow layers in the barrel and the initial atmospheric precipitation (Figure 3). Since in the winter of 2020–2021, the air temperature during the formation of 2–8 layers of the snowpack was significantly below zero (Table S2), which excluded thawing, the existence of a temperature gradient between the layers of snow is the main reason for such vertical "smoothing".

The increase in air temperature above zero after the first snowfalls leads to the first snowfalls partially or completely not staying in the snowpack because they melt and penetrate the still unfrozen surface layer of the soil. Under the condition of absence of the influence of soil moisture, it can lead to depletion of heavy isotopes in the bottom layer of the snowpack relative to the initial snowfalls, because the first snowfalls, as a rule, form at higher air temperatures and are more enriched in heavier isotopes. In our case, it is evident by comparing the bottom layer of snow formed in the barrels and directly on the earth surfaces in winter 2020–2021 (Figure 3). The melting of a part of the snowfalls from the bottom layer of the snowpack indicates that at both experimental sites (I and II, Figure 1c) located at a considerable distance from each other (~50 km) isotopic composition of the bottom layer formed on the soil surface was lighter by 3–4‰ for $\delta^{18}O$ and by 15–18‰ for δD relative to the bottom layer in the barrel and precipitation-weighted mean value of snowfalls for the same period. It should be noted that there was short-term warming (one day 11 December 2020) after the first snowfalls, and then thaws were no more in the Altai Territory until the end of February. However, at the end of November, long severe frosts were established with an even lower snowpack height, which led to deep freezing of the soil throughout the studied area, until the end of the winter. The freezing of the initially wet soil contributed to the fact that the soil moisture could not spread from the soil and condense in the bottom layer of the snowpack, which allowed us to notice the depletion in heavy isotopes of the bottom layer of the snowpack relative to the snowfalls.

Thus, the initial conditions for the snowpack formation are of great importance for the possibility of the soil moisture inflow into the bottom layer of snow. As a rule, the isotopic composition of the snow bottom layer is enriched in heavier isotopes by soil moisture; for example, Friedman et al. (1991) observed that the bottom of snow cores deposited in Fairbanks (Alaska) was enriched in heavier isotopes compared with the bulk snowpack before the beginning of the melt season [27]. The results of our work showed that the amount of soil moisture condensation in the snowpack depends on the condition of the underlying soil. Table 2 shows the data of the isotopic composition of the snowpack (bulk and separately the bottom layer) deposited on frozen and unfrozen soil in the flat part of the Altai Territory at the end of winter 2019–2020. For comparison, the table also presents the precipitation-weighted mean values of the isotopic composition of snowfalls during the same period and rainfalls within two months before the snow cover formation. The data in the table show that the average values of $\delta^{18}O$, δD, and d-excess in bulk samples of snowpack deposited on frozen and non-frozen soil practically do not differ, while the bottom layers differ distinctly. This difference for unfrozen soil can only be explained by the water transfer from the soil to the bottom layer of snow. We can estimate the isotopic composition of the soil moisture by the composition of rainfalls, which was enriched in heavier isotopes, compared with the snowfalls and had a negative d-excess (Table 2). Therefore, the input of such soil moisture can explain the change in the isotopic composition in the bottom layers of the snowpack on the non-frozen soil relative to the bulk samples, while its input is insignificant for the bottom layers on the frozen soil. The difference in the isotopic composition of the bottom layers of the snowpack on unfrozen soil is clearly shown by their local line of meteoric waters (Figure S2a, green line), the slope of which is less than the LMWL for bulk samples of snowpack and samples of the bottom layer on frozen soil.

Comparison of the isotopic composition in the bottom layers of snowpack on the frozen soil with the precipitation-weighted mean value of the isotopic composition of snowfalls over the same period (Table 2) showed that the bottom layers on frozen soil were less enriched (by 1.7‰ for $\delta^{18}O$ and by 15‰ for δD) relative to the initial atmospheric precipitation, which is in good agreement with the data for the cold season 2020–2021 (Figure 3b,d) and can be explained by the partial melting of the first snowfalls. At the same time, the deuterium excess of the bulk samples and the bottom layer of the snowpack deposited on the frozen soil indicates a weak sublimation of snow relative to the initial atmospheric precipitation.

Some studies showed that, with an increase in solar radiation for regions with solar and snow conditions similar to the Altai region, sublimation from the top layer enriches the snowpack in heavier isotopes in the daytime [29,33,43,61]; in contrast, night condensation of air moisture, which is more depleted in heavy isotopes, might fully compensate for the effects of the daytime sublimation [33,61,62]. In our opinion, before the beginning of the active snow melting, the resultant multidirectional processes of moisture exchange between the top layer of snow and the atmosphere depends on the difference between day and night temperatures. For example, in 2019–2020, the mean value of difference between day and night temperatures during the formation of the upper layer of the snowpack (No. 11) did not exceed 6 degrees (Table S2), and we noted some enrichment of snow in heavier isotopes with the decreasing of d-excess value relative to the initial snowfalls (Figure 3), that indicates the predominance of the sublimation process for this period. However, in 2020–2021, during the formation of the upper layer, the difference between day and night temperatures was already significant (mean value was 14 and max value reached 30 degrees), and the depletion in heavy isotopes of the snow layer relative to the initial snowfalls indicates the predominance of the night air moisture condensation over the process of daytime sublimation of the upper snow layer (Figure 3).

5. Conclusions

According to our results, in the cold periods of 2019–2021, the main factors controlling the change in the initial isotopic composition of water ($\delta^{18}O$ and δD) in the layers of seasonal snow cover in the south of Western Siberia are the existence of a vertical (between layers) temperature gradient, which contributes to the vertical "smoothing" of the isotopic composition within the snowpack, and the influence of soil moisture, which enriches the bottom layer of snowpack in heavier isotopes. Soil moisture has the most significant effect on the bottom layer of snowpack in contact with unfrozen soil. During the winter period, the sublimation of the upper layers of snowpack is observed only at the moment of a sharp increase in the daily air temperature. At the end of winter, with an increase in solar radiation, the contrast between day and night air temperatures determines the shift in the isotopic composition of the top layer of snowpack, relative to the initial snowfall, towards its enrichment in heavier isotopes (a temperature difference of less than 10 degrees, as per the top snow layer in 2019–2020) or depletion (a temperature difference over 15–20 degrees, as per the top snow layer in 2020–2021).

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app12020625/s1, Figure S1: Sampling site on the roof of the building of the Institute for Water and Environmental Problems of the Siberian Branch of the Russian Academy of Sciences (IWEP SB RAS) (a) Snowfall's event-based collecting; (b) getting the snow layers from a plastic barrel (experiment No.1), Figure S2: Local meteoric water lines (LMWL) for winter (a) 2019–2020 and (b) 2020–2021. Blue–event-based precipitation, black–snowpack (bulk), green-bottom layer of the snowpack on a non-frozen soil, red-bottom layer of the snowpack on a frozen soil, Table S1: The statistical estimates of LMWL for snowpack and snowfall samples getting in Altai region in winter 2019–2020 and 2020–2021 (Ordinary least squares regression (OLSR) was applied), Table S2: The daily average air temperature and difference between day and night air temperatures during the formation of layers of the snowpack (Experiment No. 1 and No. 2).

Author Contributions: Conceptualization, T.P.; methodology, T.P. and A.E.; investigation, A.E. and T.N.; writing—original draft preparation, T.P., A.E. and T.N.; writing—review and editing, T.P.; visualization, T.N. and A.E.; resources and funding acquisition, T.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Russian Foundation for Basic Research (RFBR), grant number 19-05-50057.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets used and analyzed during the current study are available from the corresponding author (Tatyana Papina) on reasonable request.

Acknowledgments: The authors are grateful to the researchers of the Institute for Water and Environmental Problems of the SB RAS Anton Kotovshchikov, Maria Panina, and Lilia Shol for their help in the field work on sampling the snowpack and Olga Lovtskaya for help in statistical analysis of regression equations.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Siegenthaler, U.; Oeschger, H. Correlation of O-18 in precipitation with temperature and altitude. *Nature* **1980**, *285*, 314–317. [CrossRef]
2. Holdworth, G.; Fogarasi, S.; Krouse, H.R. Variation of the stable isotopes of water with altitude in the Saint Elias Mountains of Canada. *J. Geophys. Res.* **1991**, *96*, 7483–7494. [CrossRef]
3. Ciais, P.; Jouzel, J. Deuterium and oxygen-18 in precipitation: Isotopic model, including mixed cloud processes. *J. Geophys. Res.* **1994**, *99*, 6793–16803. [CrossRef]
4. Clark, I.D.; Fritz, P. *Environmental Isotopes in Hydrogeology*; CRC Press/Lewis Publishers: Boca Raton, NY, USA, 1997. [CrossRef]
5. Schotterer, U.; Gäggeler, H.W.; Fröhlich, K.; Sandjordj, S.; Stichler, W. Isotope records from Mongolian and alpine ice cores as climate indicator. *Clim. Chang.* **1997**, *36*, 519–530. [CrossRef]
6. Poage, M.A.; Chamberlain, C.P. Empirical relationships between elevation and the stable isotope composition of precipitation and surface waters: Considerations for studies of paleoelevation change. *Am. J. Sci.* **2001**, *31*, 1–15. [CrossRef]
7. He, Y.; Pang, H.; Theakstone, W.H.; Zhang, D.; Lu, A.; Song, B.; Yuan, L.; Ning, B. Spatial and temporal variation of oxygen isotopes in snowpacks and glacial runoff in different types of glacial area in western China. *Ann. Glaciol.* **2006**, *43*, 269–274. [CrossRef]
8. Koeniger, P.; Hubbart, J.A.; Link, T.; Marshall, J.D. Isotopic variation of snow cover and streamflow in response to changes in canopy structure in a snow-dominated mountain catchment. *Hydrol. Process.* **2008**, *22*, 557–566. [CrossRef]
9. Berghuijs, W.R.; Woods, R.A.; Hrachowitz, M. A precipitation shift from snow towards rain leads to a decrease in streamflow. *Nat. Clim. Chang.* **2014**, *4*, 583–586. [CrossRef]
10. Bowen, G.J.; Good, S.P. Incorporating water isoscapes in hydrological and water resource investigations. *Wiley Interdiscip. Rev. Water* **2015**, *2*, 107–119. [CrossRef]
11. Kozachek, A.; Mikhalenko, V.; Masson-Delmotte, V.; Ekaykin, A.; Ginot, P.; Kutuzov, S.; Legrand, M.; Lipenkov, V.; Preunkert, S. Large-scale drivers of Caucasus climate variability in meteorological records and Mt Elbrus ice cores. *Clim. Past* **2017**, *13*, 473–489. [CrossRef]
12. Allen, S.T.; Keim, R.F.; Barnard, H.R.; McDonnell, J.J.; Brooks, J.R. The role of stable isotopes in understanding rainfall interception processes: A review. *Wiley Interdiscip. Rev. Water* **2017**, *4*, e1187. [CrossRef]

13. Delavau, C.J.; Stadnyk, T.; Holmes, T. Examining the impacts of precipitation isotope input (δ18Oppt) on distributed, tracer-aided hydrological modelling. *Hydrol. Earth Syst. Sci.* **2017**, *21*, 2595–2614. [CrossRef]
14. Vasil'chuk, Y.; Chizhova, J.; Frolova, N.; Budantseva, N.; Kireeva, M.; Oleynikov, A.; Tokarev, I.; Rets, E.; Vasil'chuk, A. A variation of stable isotope composition of snow with altitude on the Elbrus mountain, Central Caucasus. *Geogr. Environ. Sustain.* **2020**, *13*, 172–182. [CrossRef]
15. Bender, E.; Lehning, M.; Fiddes, J. Changes in Climatology, Snow Cover, and Ground Temperatures at High Alpine Locations. *Front. Earth Sci.* **2020**, *8*, 100. [CrossRef]
16. Craig, H. Isotopic Variations in Meteoric Waters. *Science* **1961**, *133*, 1702–1703. [CrossRef] [PubMed]
17. Welker, J.M. Isotopic (δ 18O) characteristics of weekly precipitation collected across the USA: An initial analysis with application to water source studies. *Hydrol. Processes* **2000**, *14*, 1449–1464. [CrossRef]
18. Froehlich, K.; Gibson, J.J.; Aggarwal, P.K. *Deuterium Excess in Precipitation and Its Climatological Significance*; IAEA: Vienna, Austria, 2002; Volume 34, pp. 54–66.
19. Liu, Z.; Tian, L.; Yao, T.; Yu, W. Seasonal deuterium excess in Nagqu precipitation: Influence of moisture transport and recycling in the middle of Tibetan Plateau. *Environ. Geol.* **2008**, *55*, 1501–1506. [CrossRef]
20. Ma, Q.; Zhang, M.; Wang, S.; Wang, Q.; Liu, W.; Li, F.; Chen, F. An investigation of moisture sources and secondary evaporation in Lanzhou, Northwest China. *Environ. Earth Sci.* **2014**, *71*, 3375–3385. [CrossRef]
21. Araguas-Araguas, L.; Froehlich, K.; Rozanski, K. Deuterium and oxygen-18 isotope composition of precipitation and atmospheric moisture. *Hydrol. Processes* **2000**, *14*, 1341–1355. [CrossRef]
22. Wu, H.; Zhang, X.; Li, X.; Li, G.; Huang, Y. Seasonal variations of deuterium and oxygen-18 isotopes and their response to moisture source for precipitation events in the subtropical monsoon region. *Hydrol. Processes* **2015**, *29*, 90–102. [CrossRef]
23. Papina, T.S.; Malygina, N.S.; Eirikh, A.N.; Galanin, A.A.; Zheleznyak, M.N. Isotopic composition and sources of atmospheric precipitation in Central Yakutia. *Earth's Cryosphere* **2017**, *2*, 60–69. [CrossRef]
24. Malygina, N.S.; Eyrikh, A.N.; Agbalyan, E.V.; Papina, T.S. Isotopic composition and source regions of winter precipitation in the Nadym Lowland Led i Sneg. *Ice Snow* **2020**, *60*, 98–108. (In Russian) [CrossRef]
25. Papina, T.S.; Eirikh, A.N.; Malygina, N.S.; Eyrikh, S.S.; Ostanin, O.V.; Yashina, T.V. Microelement and stable isotopic composition of snowpack in the Katunsky Biosphere Reserve (Altai Republic). Led i Sneg. *Ice Snow* **2018**, *58*, 41–55. (In Russian) [CrossRef]
26. Colbeck, S.C. An overview of seasonal snow metamorphism. *Rev. Geophys.* **1982**, *20*, 45–61. [CrossRef]
27. Friedman, I.; Benson, C.; Gleason, J. Isotopic changes during snow metamorphism. In *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*; Taylor, H.P., O'Neil, J.R., Kaplan, I.R., Eds.; The Geochemical Society: San Antonio, TX, USA, 1991; pp. 211–221.
28. Taylor, S.; Feng, X.; Kirchner, J.W.; Osterhuber, R.; Klaue, B.; Renshaw, C.E. Isotopic evolution of a seasonal snowpack and its melt. *Water Resour. Res.* **2001**, *37*, 759–769. [CrossRef]
29. Earman, S.; Campbell, A.R.; Phillips, F.M.; Newman, B.D. Isotopic exchange between snow and atmospheric water vapor: Estimation of the snowmelt component of groundwater recharge in the southwestern United States. *J. Geophys. Res. Atmos.* **2006**, *111*, D09302. [CrossRef]
30. Sokratov, S.A.; Golubev, V.N. Snow isotopic content change by sublimation. *J. Glaciol.* **2009**, *55*, 823–828. [CrossRef]
31. Lee, J.; Feng, X.; Faiia, A.M.; Posmentier, E.S.; Kirchner, J.W.; Osterhuber, R.; Taylor, S. Isotopic evolution of a seasonal snow cover and its melt by isotopic exchange between liquid water and ice. *Chem. Geol.* **2010**, *270*, 126–134. [CrossRef]
32. Golubev, V.N.; Konishchev, V.N.; Sokratov, S.A.; Grebennikov, P.B. Influence of sublimation in a seasonal snow cover on formation of an isotopic content of wedge ice. *Kriosf. Zemli. Earth's Cryosphere* **2001**, *3*, 71–77. (In Russian)
33. Beria, H.; Larsen, J.R.; Ceperley, N.C.; Michelon, A.; Vennemann, T.; Schaefli, B. Understanding snow hydrological processes through the lens of stable water isotopes. *Wiley Interdiscip. Rev. Water* **2018**, *5*, e1311. [CrossRef]
34. Chizhova, Y.N.; Vasilchuk, J.Y.; Yoshikava, K.; Budantseva, N.A.; Golovanov, D.L.; Sorokina, O.I.; Stanilovskaya, Y.V.; Vasilchuk, Y.K. Isotopic composition of the snow cover of the Baikal region. *Ice Snow* **2015**, *3*, 55–66. [CrossRef]
35. Vasilchuk, Y.K.; Shevchenko, V.P.; Lisitsyn, A.P.; Budantseva, N.A.; Vorobiev, S.N.; Kirpotin, S.N.; Kritskov, I.V.; Manasypov, R.M.; Pokrovsky, O.S.; Chizhova, J.N. Oxygen-isotope and deuterium composition of the snow cover of Western Siberia on the profile from Tomsk to the Gulf of Ob. *Dokl. Akad. Nauk.* **2016**, *471*, 1284–1287. (In Russian) [CrossRef]
36. Wever, N.; Comola, F.; Bavay, M.; Lehning, M. Simulating the influence of snow surface processes on soil moisture dynamics and streamflow generation in an alpine catchment. *Hydrol. Earth Syst. Sci.* **2017**, *21*, 4053–4071. [CrossRef]
37. Ren, W.; Yao, T.; Yang, X.; Joswiak, D.R. Implications of variations in δ18O and δD in precipitation at Madoi in the eastern Tibetan Plateau. *Quat. Int.* **2013**, *313*, 56–61. [CrossRef]
38. Motoyama, H.; Hirasawa, N.; Satow, K.; Watanabe, O. Seasonal variations in oxygen isotope ratios of daily collected precipitation and wind drift samples and in the final snow cover at Dome Fuji Station, Antarctica. *J. Geophys. Res. Atmos.* **2005**, *110*, D11106. [CrossRef]
39. Eiriksson, D.; Whitson, M.; Luce, C.H.; Marshall, H.P.; Bradford, J.; Benner, S.G.; McNamara, J.P. An evaluation of the hydrologic relevance of lateral flow in snow at hillslope and catchment scales. *Hydrol. Processes* **2013**, *27*, 640–654. [CrossRef]
40. Evans, S.L.; Flores, A.N.; Heilig, A.; Kohn, M.J.; Marshall, H.-P.; McNamara, J.P. Isotopic evidence for lateral flow and diffusive transport, but not sublimation, in a sloped seasonal snowpack, Idaho, USA. *Geophys. Res. Lett.* **2016**, *43*, 3298–3306. [CrossRef]

41. Biederman, J.A.; Brooks, P.D.; Harpold, A.A.; Gochis, D.J.; Gutmann, E.; Reed, D.E.; Pendall, E.; Ewers, B.E. Multiscale observations of snow accumulation and peak snowpack following widespread, insect-induced lodgepole pine mortality. *Ecohydrology* **2014**, *7*, 150–162. [CrossRef]
42. Biederman, J.A.; Harpold, A.A.; Gochis, D.J.; Ewers, B.E.; Reed, D.E.; Papuga, S.A.; Brooks, P.D. Increased evaporation following widespread tree mortality limits streamflow response. *Water Resour. Res.* **2014**, *50*, 5395–5409. [CrossRef]
43. Gustafson, J.R.; Brooks, P.D.; Molotch, N.P.; Veatch, W.C. Estimating snow sublimation using natural chemical and isotopic tracers across a gradient of solar radiation. *Water Resour. Res.* **2010**, *46*, W12511. [CrossRef]
44. Mott, R.; Schirmer, M.; Bavay, M.; Grünewald, T.; Lehning, M. Understanding snow-transport processes shaping the mountain snow-cover. *Cryosphere* **2010**, *4*, 545–559. [CrossRef]
45. Comola, F.; Kok, J.F.; Gaume, J.; Paterna, E.; Lehning, M. Fragmentation of wind-blown snow crystals. *Geophys. Res. Lett.* **2017**, *44*, 4195–4203. [CrossRef]
46. Essery, R.; Li, L.; Pomeroy, J. A distributed model of blowing snow over complex terrain. *Hydrol. Processes* **1999**, *13*, 2423–2438. [CrossRef]
47. State Report. *On the State and Environmental Protection in the Altai Territory in 2019*; Cyberleninka: Barnaul, Russia, 2020; p. 200. (In Russian)
48. Kharlamova, N.; Kazartseva, O. Distribution of snow storage in the Altai territory. *Bull. Sci. Pract.* **2017**, *4*, 162–169. (In Russian)
49. Belyaev, V.I.; Sokolova, L.V. The evaluation of the agroclimatic potential of the Altai region. *Vestn. Altayskogo Gos. Agrar. Univ.* **2020**, *12*, 59–64.
50. Gefke, I.V.; Aleshina, N.I. Physical and geographical characteristics upper Obi basin. *Int. J. Humanit. Nat. Sci.* **2019**, *11–12*, 61–63. [CrossRef]
51. Nikolchenko, Y.N.; Sukhova, M.G. Wind energy potential of Altai territory as component of sustainable development in region. *Bull. Tambov Univ.* **2013**, *18*, 663–667.
52. Kharlamova, N.F.; Kozlova, D.S. Statistical Characteristics of Atmospheric Precipitation Regime in the Altai Region. *Izvestiya AltGU—News Altai State Univ.* **2014**, *83*, 145–150. (In Russian) [CrossRef]
53. Filimonov, V.Y.; Baldakov, N.A.; Kudishin, A.V.; Lovtskaya, O.V. The correlation analysis of seasonal runoff and snow reserves in large tributaries of the upper Ob. *Interexpo Geo-Siberia* **2018**, *1*, 284–294. (In Russian)
54. Sturm, M.; Holmgren, J.; Liston, G.E. A seasonal snow cover classification-system for local to global applications. *J. Clim.* **1995**, *8*, 1261–1283. [CrossRef]
55. Maksimova, N.B.; Arnaut, D.V.; Morkovkin, G.G. The dynamics of moisture availability in the agro-climatic areas of the Altai region. *Bull. Altai State Agrar. Univ.* **2016**, *5*, 77–81. (In Russian)
56. Report. *On the State and Environmental Protection of the City District—The City of Barnaul in the Altai Territory in 2018*; Cyberleninka: Barnaul, Russia, 2019; p. 141. (In Russian)
57. Dansgaard, W. Stable isotopes in precipitation. *Tellus* **1964**, *16*, 436–468. [CrossRef]
58. Taylor Jonh, R. *An Introduction to Error Analysis*, 2nd ed.; University Science Books: Sausalito, CA, USA, 1997; p. 349.
59. Winograd, I.J.; Riggs, A.C.; Coplen, T.B. The relative contributions of summer and cool-season precipitation to groundwater recharge, Spring Mountains, Nevada, USA. *Hydrogeol. J.* **1998**, *6*, 77–93. [CrossRef]
60. Unnikrishna, P.V.; McDonnell, J.J.; Kendall, C. Isotope variations in a Sierra Nevada snowpack and their relation to meltwater. *J. Hydrol.* **2002**, *260*, 38–57. [CrossRef]
61. Stichler, W.; Schotterer, U.; Fröhlich, K.; Ginot, P.; Kull, C.; Gäggeler, H.; Pouyaud, B. Influence of sublimation on stable isotope records recovered from high-altitude glaciers in the tropical Andes. *J. Geophys. Res.—Atmos.* **2001**, *106*, 22613–22620. [CrossRef]
62. Schlaepfer, D.R.; Ewers, B.E.; Shuman, B.N.; Williams, D.G.; Frank, J.M.; Massman, W.J.; Lauenroth, W.K. Terrestrial water fluxes dominated by transpiration: Comment. *Ecosphere* **2014**, *5*, 61. [CrossRef]