

Article



Seasonal Variability and Evolution of Glaciochemistry at An Alpine Temperate Glacier on the Southeastern Tibetan Plateau

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Abstract: Temperate glaciers are highly sensitive to climatic and environmental changes. Studying the chemical composition of snow, firn, and ice on temperate glaciers is important for understanding the variations in atmospheric circulation patterns, deposition conditions, and melting processes. To define snowpack chemistry and environmental significance, seven snowpacks (one snowpack in late autumn, two in winter, two in spring, and two in summer) were sampled in 2008/2009 on Baishui Glacier No. 1 in Mt. Yulong. Soluble ions in the winter snowpacks showed low values in the middle part but high values in the lower and upper parts, influenced by the atmospheric deposition of snow accumulation. The larger variations of ionic concentrations in the spring snowpacks were associated with the variable atmospheric patterns with high dust content in spring, leading to high ionic concentrations in the upper snowpack. Strong meltwater percolation resulted in quick migration and redistribution of ions for the profiles during the monsoon period. The ion elution sequence was $Ca^{2+} > SO_4^{2-} > NH_4^+ > K^+ > NO_3^- > Na^+ > Cl^- > Mg^{2+}$. Factor analysis showed that NO_3^- , SO_4^{2-} , NH_4^+ were mainly supplied by wet deposition-plus-anthropogenic input, while Cl^- and Na^+ originated from marine sources. Ca²⁺ and Mg²⁺ had multiple sources and the local terrestrial source was important because of locally exposed carbonate. The results suggest that chemical concentrations reflect mainly impurities supplied by atmospheric circulation and precipitation during periods of snow accumulation, as well as during the melting process.

Keywords: Baishui Glacier No. 1; glaciochemistry; Mt. Yulong; snowpacks

1. Introduction

Yulong Snow Mountain (Mt. Yulong), located on the Tibetan Plateau (TP), is one of the high mountain glacial areas and is a natural laboratory for environmental sciences. These are temperate alpine glaciers that are sensitive indicators of climate change. Temperate glaciers are ideal regions for studying the chemical composition changes in snow, firn, and ice because temperate glaciers are highly sensitive to climatic and environmental changes. Snowpack chemistry can characterize different atmospheric circulation patterns and is markedly characterized by different atmospheric circulations in a year. Analysis of the chemical composition of snow and ice is one of the most important areas in glaciology [1–3]. Specifically, environmental chemistry provides a valuable tool for better understanding the sources of atmospheric aerosols [4–6], atmosphere circulation [7–9], and past climatic and environmental changes [10,11]. Snowmelt-dominated environments of high

altitude are sensitive to variations in chemical composition of atmospheric deposition, which is critical in understanding regional air pollution and its effects on hydrologic systems [12,13]. Data available from studies that have utilized the precipitation, snow, and ice chemistry have contributed to our understanding of environmental signals from different regions of the globe [14–19]. Detailed stratigraphic records of the ionic composition in snowpacks not only reflect the condition of atmospheric deposition and climatic conditions but also provide important information for studying ice core records [9]. Therefore, the characteristics of the chemical content of snow, as well as its distribution and evolution in snowpacks on glaciers, are of high significance.

In general, the concentrations of soluble species in snow and ice have been shown to display a correlation with the atmospheric deposition conditions, particularly temperature, amount of precipitation, and the associated air-mass trajectories and source regions [20,21]. With regard to the available spatial coverage of snow, snowpacks, and ice records, the data on ionic records is, as yet, inadequate to document climate and environmental changes over the vast Asian continent [9]. Mt. Yulong is an ideal region for studying the chemical composition of snow, firn, and ice because (a) Mt. Yulong is located at the southeastern Tibetan Plateau and is at the transition zone from the plateau to the Himalayan range; (b) modern temperate glaciers distribute in Mt. Yulong, which is located at the southern Hengduan mountains of China (these glaciers are highly sensitive to climate and environmental changes [22]); (c) the seasonal changes in atmospheric circulations result in marked seasonal variations of the chemical content in the precipitation and snowpacks.

Snow/firn-core records have been previously investigated in the Mt. Yulong region [23,24]. Although the 10.10 m firn core of Baishui Glacier No. 1 sampled in 1999 is strongly influenced by meltwater, it still could provide climatic records [25]. Studies on a firn profile from the accumulation area of the largest glacier, Baishui No. 1, in Mt. Yulong have suggested that the chemical species in the snow and firn on Mt. Yulong originate from three different sources: marine, crustal, and anthropogenic sources [26]. Li et al. [27] indicated that the snow sampled in May 2006 at both 4900 and 4750 m on Baishui Glacier No. 1 was deposited in different seasons since they showed distinct ionic compositions. Niu et al. [17] noted changes in the surface snowpack chemistry (e.g., Ca²⁺, Mg²⁺), mainly transported from Central Asia through the south limb of the westerlies in non-monsoon seasons. The southeast monsoon is the prevailing air mass in the Mt. Yulong region during the monsoon season and accounts for the extensive precipitation and lower snow ion concentrations in this season. However, the studies conducted on Mt. Yulong have not looked at the seasonal evolution of snow and snowpack levels in a year to date. A detailed analysis is needed to better understand the effects of depositional processes and meltwater-related post-depositional processes on chemical species in the snowpack. The main objective of this research is to determine the seasonal variability (over a year) and the elution processes of the major ionic concentrations in snowpacks, as well as investigate the environmental significance of these chemical records. Such a study is vital for providing important insight into environmental evolution within the regional basin, as well as over the Asian continent.

2. Study Area

Mt. Yulong $(27^{\circ}10'-27^{\circ}40' \text{ N}, 100^{\circ}09'-100^{\circ}20' \text{ E}, 5596 \text{ m}. a.s.l.)$ is located on the southeast Tibetan Plateau, China. There are 15 glaciers on the mountain that cover an area of 7.65 km². The Baishui Glacier No. 1, the largest glacier on this mountain, is 2.26 km long with an area of 1.32 km². Its accumulation area is relatively flat and extends for ~1 km² (Figure 1). Crevasses are widespread on the glacier tongue. The elevations of the equilibrium line (ELA) and the glacier front are 4800 and 4365 m, respectively. The ELA receives a total mean annual precipitation of 2000 mm and has a recorded mean annual temperature of $-3.7 \,^{\circ}\text{C}$ [28,29]. Usually, snow accumulates between October and May over Mt. Yulong. This differentiates the glacier from most Himalayan glaciers that are summer accumulation-type and dominated by the summer monsoon in the wet season. It is difficult to sample a snowpack after July because of factors such as high temperature, liquid precipitation, and intense ablation in the monsoon season. The monthly mean temperature of ELA was lower than

0 °C from November to April and higher than 0 °C from May to October. Thus, intense melting occurred since May (Figure 2).



Figure 1. Location of the snowpack of the Baishui Glacier No. 1 in Mt. Yulong.



Figure 2. Monthly mean temperature from October 2008 to September 2009 at 4800 m on Baishui Glacier No. 1.

Situated at the southeastern edge of the Qinghai-Tibetan Plateau, the Baishui Glacier No. 1 has a complex environment influenced by variable atmospheric circulations. The region is characterized by a monsoon climate. The Indian monsoon results in abundant rains during the wet season (from May/June to October), while the south branch of the west wind brings dry and warm air in an arid climate (from November to the following April) [30]. Seasons are defined as traditional spring, summer, autumn, and winter. Winter (from mid-November to February) is dominated by the westerly jet with moisture being transported across Central Asia; spring (from March to May) is dominated by complex circulations from the Qinghai–Tibetan Plateau region and local circulations; the summer monsoon period (from June to August) is dominated by the southeast and southwest monsoon; the autumn (post-monsoon) period (from the middle of September to November) is dominated by complex circulations as a second transition period.

3. Materials and Methods

Between November 2008 and July 2009, a snowpack was excavated at the ELA (27.33° N, 100.25° E, 4800 m) of Baishui Glacier No. 1 each month with the exception of February and May. Non-particulating suits, polyethylene gloves, and masks were worn to ensure that the samples were not contaminated during collection and handling.

We sampled the entire snowpack at 10-cm increments. Snowpack samples were taken into polyethylene containers that had been pre-washed with ultra-pure water. All samples were kept frozen and transported to the State Key Laboratory of Cryospheric Science, Cold and Arid Regions

Environment and Engineering Research Institute, Chinese Academy of Sciences for testing. Five samples were lost during the transportation, of which two were sampled in January and three were sampled in June. In addition, field blanks were collected, filled with ultra-pure water in the laboratory, opened during sample collection, and handled as samples. Analysis of field blank samples indicated that sample contamination during collection, transport, and subsequent analytical procedures was negligible. All snow samples were analyzed immediately after melting. Cations (NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺) were analyzed with a Dionex-DX320 ion chromatograph whereas anions were analyzed (F^- , Cl⁻, NO₃⁻, SO₄²⁻) with a Dionex-ICS1500 ion chromatograph. The analytical precision reached 10^{-9} g/mL and the standard deviation was <5%.

Temperature data were collected by automatic weather stations (AWS, Campbell Company, Camden, NJ, USA) at an altitude of 4800 m on Baishui Glacier No. 1.

4. Results and Discussion

4.1. Chemical Composition of Snowpack Samples

The mean ion concentrations for the snowpack samples collected from Baishui Glacier No. 1 on the eastern slope of Mt. Yulong are presented in Table 1. Snow depths for all seven snowpacks ranged from 0.64 to 3.02 m. The dominant cation was Ca²⁺, having far higher concentrations than the other species. The dominant anion analyzed was SO₄²⁻. However, SO₄²⁻ was not the dominant anion in the snow. According to the ionic balances ΔC (total cation equivalents minus total anion equivalents) for the snowpack samples, the average (51.4 meq·L⁻¹) accounted for 78% of the total ion content, reflecting a large excess of cations in the snowpit samples. Linear regression shows that the calcium and ΔC correlated well (R² = 0.99, N = 131, *p* < 0.01), suggesting that the ΔC represents primarily the carbonate/bicarbonate in the snow [31]. Thus, the carbonate/bicarbonate should be the dominant anion, which was also illustrated by Pang et al. [26]. The mean concentration of SO₄²⁻ and NO₃⁻ in the snowpack was higher than the mean value in a 10.3 m firn profile, which had seven complete annual layers (1997–2003), indicating the increasing anthropogenic input in this century [26].

Month		November	December	January	March	April	June	July
N.		17	15	11	26	31	27	7
Depth (cm)		158	140	120	250	302	262	64
pH		6.27	6.91	6.51	6.69	6.88	6.49	6.51
EC		3.39	3.15	8.07	11.05	11.61	6.19	3.52
Cl-	Mean	0.01	0.01	0.02	0.05	0.06	0.14	0.04
	Dev.	0.01	0.01	0.01	0.07	0.05	0.16	0.05
NO ₃ -	Mean	0.05	0.04	0.06	0.38	0.33	0.09	0.05
	Dev.	0.07	0.03	0.05	0.53	0.30	0.12	0.03
SO4 ²⁻	Mean	0.06	0.04	0.09	0.80	0.71	0.15	0.06
	Dev.	0.07	0.04	0.06	1.05	0.70	0.24	0.02
Na ⁺	Mean	0.00	0.00	0.00	0.02	0.04	0.11	0.02
	Dev.	0.00	0.00	0.01	0.03	0.08	0.17	0.04
NH4 ⁺	Mean Dev.	0.01 0.01	0.01 0.01	0.03 0.02	0.17 0.23	0.15 0.13	0.05 0.06	0.03 0.01
K ⁺	Mean	0.01	0.00	0.01	0.06	0.06	0.06	0.02
	Dev.	0.01	0.00	0.01	0.09	0.06	0.08	0.03
Mg ²⁺	Mean	0.03	0.03	0.08	0.08	0.06	0.04	0.05
	Dev.	0.05	0.05	0.09	0.09	0.06	0.05	0.04
Ca ²⁺	Mean	0.45	0.44	1.53	2.08	2.06	0.80	0.45
	Dev.	0.79	0.64	2.20	2.39	2.11	1.17	0.23

Table 1. Major ion concentrations (mg/L) of the snowpack samples from Baishui Glacier No. 1 in Mt. Yulong (bolded values are high ionic concentration).

Note: "N." stands for the number of samples, "Dev." stands for the standard deviation.

Comparison of the ion concentrations among the seven snowpits shows that the ionic concentrations of the snowpacks were variable in different months. The seasonal variations may have resulted from many factors, such as atmospheric circulation, atmospheric fall-out impurities, precipitation sources, and lateral transport of meltwater [23,27]. Another feature of snowpack chemistry is that, except for Ca^{2+} concentrations, cations show somewhat less variability than anions. The mean ionic concentration of the snowpack profile was higher in the spring than in the other months, which is consistent with results from snowpacks from the Himalayas [32] and chemical records from Dasuopu Shallow Ice Core [33–35]. This may have been caused by Asian dust storm-derived aerosol input and other aerosols entrained in precipitation [31]. Na⁺ and Cl⁻ peaked in the summer as monsoon circulation led to a moisture source from the Indian Ocean. The mean concentration of Ca^{2+} in the snowpack increased from January to April and decreased from April to June, which was related to the local lithology. Limestone is the most abundant lithology in the region and a major source of alkalinity, resulting in the high concentration of Ca^{2+} in the spring. The mean concentration of Ca^{2+} in the snowpack sampled in 2014 was lower than that sampled in 2006 [27], indicating different input from the local terrestrial sources in different years.

Chemical variations for the major ion concentrations versus depth for the seven snowpits are apparent. As shown in Figure 3a, there were low values in the middle part of the profile, between 0.50 m and 1.20 m, and high values in the lowermost part of the snowpack profile sampled on 9 November. Concentrations tended to decrease from this maximum to 1.2 m and then increase in the upper part. The distributions of ions may be related mainly to the atmospheric circulation during snow accumulation. Higher concentrations of ions in the lower part indicate that melting of snow occurred at the end of the ablation season, which caused the elution of ions from the upper layer of the snowpack with subsequent enrichment of the deeper part with the downward migration and redistribution by the percolating water. The snowpack sampled in December and January showed a similar distribution of ions, while the layer maximum value appeared to be nearer to the bottom of the snowpack as a result of the downward ion transportation (Figure 3b,c).



Figure 3. Cont.





Figure 3. The vertical variation of ionic concentrations for snow profiles sampled in (**a**) November, (**b**) December, (**c**) January, (**d**) March, (**e**) April, (**f**) June, and (**g**) July.

The relatively large amplitude variations of ionic concentrations occurred in the snowpack sampled in spring (March and May). The distribution of ions between 0.0 and 1.5 m was similar to the profile variation of the snowpack in November, December, and January but showed a great difference above 1.5 m, suggesting specific atmospheric fall-out impurities in the spring. Concentrations in the upper part of the profile were generally high. This may be attributed to the variable atmospheric patterns with a high dust content in the spring. Winter (from mid-November to February) is dominated by the westerly jet with moisture being transported across Central Asia, while spring (from March to May) is dominated by complex circulations from the Qinghai–Tibetan Plateau region and from local circulation. This is also illustrated by Li et al. [27]. The maximum values for the March snowpack appeared at depths of 1.6 m and 2.4 m. The values between the two layers were relatively low but were relatively high in the lowermost part of the snowpack (Figure 3d). Moreover, the layer's maximum values appeared below 1.5 m in April, and ion concentrations show a decreasing trend from the maximum to the surface layer (Figure 3e). This indicates that the atmospheric circulation/moisture sources were variable in April and that snow in the upper part of the two snowpacks experienced little elution of ions and downward migration due to the faint melting of snow compared with the ablation season.

As the temperature increased in spring and summer (Figure 2), the melting of snow was stronger, leading to a sharp downward migration and redistribution of ions. As for the 14 June snowpack (Figure 3f), ion distributions were significantly different from the snowpack sampled in April. Concentrations of sulfate (SO_4^{2-}) and nitrate (NO_3^{-}) were low in the lower part, between 0.00 m and 2.00 m, and high in the upper part of the profile (above 2.00 m) with maximum values appearing at a depth of 2.10 m. Ammonium (NH_4^+) showed a similar distribution. As for potassium (K^+), sodium (Na^+), and chloride (Cl^-) ions, the concentrations were low in the middle part of the profile, between 1.00 m and 1.50 m, and increased sharply from 1.00 m to the bottom, which was greatly different from the variations of the snowpack sampled in pre-monsoon (spring). Concentrations above 1.50 m were

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high but the values were relatively low compared with the lowermost part of the snowpack. The redistribution of ions in the lowermost part may have been caused by the removal of soluble ions from the upper part layers of the pre-monsoon snowpack with high ion concentrations. Ions in those layers transferred downward quickly by the percolating water, redistributed, and enriched in the lower part of the snowpack during the ablation season. Maximum values appeared at a depth of about 0.5 m. The layer at 0.5 m was characterized by relatively high values for the concentration of calcium and magnesium ions. However, the maximum values of the two ions appeared in the upper part, above 2.00 m, suggesting high concentrations of Ca^{2+} and Mg^{2+} in the surface snow, which was mainly contributed to by the local atmospheric pattern. It is noted that the ionic concentrations in the upper part were higher than those in the middle and lower parts. This indicates that melting of the snow at the surface had caused an increase in the mean concentration of ions in the upper part of the pack but that the percolation of meltwater had not carried the ions down to the middle part. However, little variation of ion concentrations was examined in the 3 July snowpack (Figure 3e), which may be related to homogenization, resulting from the strong melting of snow during the monsoon ablation season.

Overall, the ionic concentrations in the snowpacks sampled from November to April can reflect the atmospheric input. The rate of snow accumulation was high for temperate glaciers and ablation was especially strong compared with continental glaciers during the ablation period [31]. Strong percolation of meltwater led to quick migration and redistribution of ions for the snowpack profile in the monsoon period. The maximum of different ions appeared at the different layers in the snowpacks, indicating different migration rates for the ions.

4.2. Elution Process

For most low- to mid-latitude mountain glaciers, snow is transformed to ice through meltwater infiltration and refreezing. As meltwater infiltrates downwards to the bottom of a snowpack, elution occurs and the chemical species within the firn are redistributed by differential transportation toward the base of the snowpack [31]. Previous studies have suggested that ions are leached from snow and firn with different efficiencies that depend on specific characteristics of the chemical species, such as ablation and elution rates [31]. It is important to observe the elution sequence and establish the effects of preferential elution as a snowpack melts [36–38]. Assuming that the surface snow in the region of the series of snowpits was chemically homogeneous and that the input of dry deposition was small, preferential elution sequences could then be derived during a period of ablation [36].

The preferential elution sequences are assumed to be independent of concentration and the history of melting and refreezing according to previous assumptions [36]. Therefore, the elution sequence of ions was determined by comparing the ratio of each ion concentration (in the initial surface to that found on resampling). As explicit changes occurred from 19 March to 17 June 2009, this was selected as the study period for this work. For analyzing the elution sequence, a commonly used statistical model was adopted as follows: $N_i = (X_i - X_{min})/(X_{max} - X_{min})$, where N_i , X_i , X_{max} , and X_{min} are the standard values, the average value of ion concentration in the snowpack, and the maximum and minimum value of ion concentration corresponding to the snowpack, respectively. Dealing with the data by linear fitting and by comparing these slopes, the following elution sequence of the chemical species was obtained: $Ca^{2+} > SO_4^{2-} > NH_4^+ > K^+ > NO_3^- > Na^+ > Cl^- > Mg^{2+}$. The present work suggests that calcium appears earlier in the sequence and that chloride is less mobile than ammonium. Many studies have demonstrated that soluble ions are leached from snow and firn with different efficiencies [10,31,36–38]. The rapid leaching of solutes during the first phase of snow melting is advantageous for explaining glaciochemical records in ice cores. As a result, the ion elution sequence has been investigated in various field and laboratory studies. Sequences have been measured by laboratory experiments, such as $SO_4^{2-} > Mg^{2+} \sim Ca^{2+} > K^+ > Na^+ > NO_3^- > NO_3^-$ Cl⁻ by the chromatographic process to explain the preferential elution of inorganic ions observed in water from melting snowpacks [39], $SO_4^{2-} > Mg^{2+} > Na^+ \sim NO_3^- > Cl^-$ under controlled laboratory conditions [37], and $SO_4^{2-} > NO_3^{-} > K^+ > Ca^{2+} > Mg^{2+} > Na^+ > Cl^-$ through the snowpack of a small,

remote, high-altitude Scottish catchment [10]. According to field investigations, the sequences are as follows: $SO_4^{2-} > Ca^{2+} \sim Mg^{2+} > K^+ \sim Na^+ > NO_3^- > Cl^-$ at the upper part of the Grenzgletscher [38] and $SO_4^{2-} > Ca^{2+} > Na^+ > NO_3^- > Cl^- > K^+ > Mg^{2+}$ in Tien Shan [31]. In this paper, it is clear that the ion elution sequence was different from the field and laboratory studies. The result suggests that the leaching selectivity of anions is consistent with the result of previous studies: $SO_4^{2-} > NO_3^- > Cl^-$ [23,31,38]; namely, the sulfate ion was easier to leach. However, the cation elution sequence demonstrates that $Ca^{2+} > NH_4^+ > K^+ > Na^+ > Mg^{2+}$, which is different to the previous research results. In general, the ion elution sequence is affected by many factors: for instance, the initial ion concentrations in the snow, the melting intensity, the additional impurity (or rainfall) input into the snowpack, and, eventually, the snow-firn texture [31]. Therefore, the ion elution sequence does not only reflect the elution process but also reflects the dynamic equilibrium between the ions' input (wet–dry deposition) and output (elution process).

To illustrate the elution process of soluble species, we took Ca²⁺ as an example. Two apparent high peaks (Figure 3a,b) of Ca^{2+} were traced in the top and bottom of the snow-firn pack in the fall (9 November 2008). The distance of the peaks was about 120 cm (9 November 2008) and presented a small change during winter (8 January 2009), indicating that ions moved downward slowly until merging into superimposed ice. The peak B in the uppermost part of the November snowpack moved downward from 150 cm to 20 cm by 19 March 2009, and then to ice at the bottom by 17 April 2009. It is of great interest that peaks of soluble species showed significant variation during spring and summer compared with later fall and winter snowpacks. The peaks of Ca²⁺ (Figure 3c,d) suddenly appeared in the uppermost part of the snow-firn pack, above A and B, as the broken lines point (Figure 3) from 19 March to 17 April. This was mainly related to small precipitation events, low temperatures (always below zero), and weak evaporation during this period, which enabled post-depositional processes such as sublimation and dry deposition to become more dominant [40,41]. Especially, little melt occurred under the condition, which partially contributed to high values of Ca²⁺ and other major ions in the surface of the snowpit. The air temperature increased from March and was above zero in May, which would have led to significant snow melting. In the ablation season, the depth of the surface snow decreased sharply. As a large amount of meltwater infiltrated downward, the chemical species within the firn were redistributed by differential transportation toward the base of the snowpack. Simultaneously, ion concentration peaks moved downward rapidly to the lower part of the snowpack. As shown in Figure 3, the peak C above 1.6 m in the 19 March snowpack moved downward to a height of 0.5 m by 14 June and to a height of 0.4 m by 3 July. The peak D on 19 June moved downward from 2.3 m to 0.4 m by 3 July. The melting rate was 0.076 cm/day during this period. This movement was mainly related to strong snow melting and compaction during the ablation period.

4.3. Ion Source

The interrelationship of the chemical species in the snowpack was investigated using correlation matrices (Table 2). As Table 2 indicates, the aerosol ions $(NO_3^-, NH_4^+, and SO_4^{2-})$ were all well correlated across all samples (r > 0.99) with SO₄²⁻ and NO₃⁻ having the strongest correlation (r = 1.00) of any ion pair in the snowpack (Table 2). There was a significant relationship between Cl⁻ and Na⁺ (Table 2) indicating their common source, which is consistent with results from a shallow firn profile sampled in Baishui Glacier No. 1 [26]. Additionally, the following were highly correlated in the snowpack: NO₃⁻ and NH₄⁺, SO₄²⁻ and Ca²⁺, NH₄⁺ and SO₄²⁻, and Ca²⁺ and NH₄⁺. This is different from the relationship of ions in the snowpack in the Tien Shan region [31].

Ions	Cl-	NO ₃ ⁻	SO_4^{2-}	Na ⁺	NH4 ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Cl-	1							
NO_3^-	0.210	1						
SO_4^{2-}	0.207	1.000 **	1					
Na ⁺	0.991 **	0.131	0.130	1				
NH_4^+	0.290	0.993 **	0.993 **	0.207	1			
K^+	0.770 *	0.777 *	0.776 *	0.715	0.823 *	1		
Mg ²⁺	-0.007	0.582	0.583	0.127	0.618	0.362	1	
Ca ²⁺	0.140	0.873 *	0.878 **	0.050	0.883 **	0.642	0.832 *	1

Table 2. The correlation matrix for ion concentrations in Mt. Yulong snowpits.

Note: * *p* < 0.05, ** *p* < 0.01.

The correlations among the elements were further investigated using factor analysis (Table 3). Factor 1 loadings were highest for NO_3^- , SO_4^{2-} , NH_4^+ , and K^+ , accounting for 57.6% of the total variance in the major ion series. This factor was interpreted as a wet deposition-plus-anthropogenic input component, suggesting that the origin and trajectory of the air mass may be a key factor in determining the composition of precipitation across the study site. High correlations of these non-lithic ions support their similar sources. Generally, NO_3^- and SO_4^{2-} in precipitation are primarily derived from acid aerosols that are formed in the atmosphere as a result of reactions involving oxides of nitrogen (NO_x) and sulfur (SO_2) from industrial and vehicle emissions and from the burning of fossil fuels [12,13]. Pang et al. [26] indicated that NO_3^- , SO_4^{2-} , and NH_4^+ in the snow in Mt. Yulong area probably derived from anthropogenic sources, and were transported to the area by the India southwest monsoon in summer and by the south branch of the westerlies in winter. Moreover, the tourism to Mt. Yulong has seen steady growth since 1996. It was reported that Lijiang has transformed from an agricultural city (mainly primary industry) to a tourist city (mainly tertiary industry) between 1990 and 2006. In order to develop tourism, secondary industries related to heavy pollution have developed slowly [16]. The regional pollution is being vertically transported from low elevations to the alpine zone by mountain-valley winds. Besides, convective mixing of the atmosphere occurs as snow surface temperatures increase in spring. This led to the high concentrations of SO₄²⁻, NO₃⁻, and NH₄⁺ in the upper portions of the spring snowpack at the sampling sites, which is similar to the patterns observed in many studies of alpine snowpack chemistry [13,32,42].

Ions		Factor	
10115	1	2	3
Cl-	0.627	0.723	0.100
NO_3^-	0.905	-0.307	-0.137
SO_4^{2-}	0.888	-0.311	-0.226
Na ⁺	0.424	0.877	0.136
NH_4^+	0.882	-0.276	-0.288
K^+	0.905	0.315	-0.047
Mg^{2+}	0.734	-0.248	0.485
Ca ²⁺	0.716	-0.357	0.493
Variance %	57.604	21.010	8.704

Table 3. Factor loading matrix for the elements in snow.

Factor 2 loadings were highest for Cl^- and Na^+ , accounting for 21.0% of the total variance in the major ion series. This factor represents a marine source transported to the area by the southwest monsoon [31]. Factor 3 accounted for 8.7% of the total variance and was loaded with Ca^{2+} and Mg^{2+} . The two elements were also significantly linearly correlated (Table 3), suggesting that Factor 3 can be interpreted as a local terrestrial source component. Carbonate mineral dust from the local terrain is the dominant source of these ions in the snowpack since exposed carbonate is widely distributed in

the region. As strong mountain and valley winds prevail during spring along with a more regional Asian dust flux, crustal mineral aerosols enriched with Ca^{2+} and Mg^{2+} entrain in the atmosphere and are deposited in the snow, resulting in the high calcium and magnesium concentrations in the snow, snowpits, and ice cores in glacial regions [25,43].

In particular, Ca^{2+} and Mg^{2+} have more potential sources than other species. Ca^{2+} had a high loading on factor 1 (0.716) and 3 (0.493). According to correlation analysis, Ca^{2+} is highly correlated with aerosol ions, suggesting that long-distance sources are also a major contributor. It is noted that the factor 1 loadings are attributed to anthropogenic sources, which is different to the previous result [26] indicating that by 2009 human activities had influenced the environment.

4.4. Environmental Significance of Chemical Ions in Snowpack

The percolation of meltwater may cause the removal of soluble ions from the snowpack in the ablation season. It has been recognized for many years that the first fraction of meltwater from a melting snowpack contains a much higher concentration of ions than that of the bulk (or average) snow of which the pack is composed [10], presenting a large influence of the meltwaters and the original snowpack on the chemical composition. Seven months of snow research in Mt. Yulong provides evidence for studying this problem. In the June profile at the sampling site, all ions displayed high concentrations with a relatively large amplitude variation in the upper part, generally between 2.0 m and surface snow, as a result of the downward migration of meltwater. Otherwise, high values of K⁺, Na⁺, and Cl⁻ were concentrated in the lower part in the June profile, suggesting apparent removal differences between the group ions and other ions. The maximum value of each ion appeared at different depths, indicating that the ions leaching from the overlying melting snow had different removal rates. Strong meltwater percolation occurred in the June profile, leading to little vertical variation of ionic concentration. Since much snow had already melted or evaporated in the ablation period, the impurities from the meltwater had percolated into the lower part of the snowpack and had concentrated there, blocked by the ice layers [44].

Chemical records from different seasons of a glacier may provide different environmental information [2,13]. Ionic concentrations in the slightly-melting snow during non-ablation season gives information mainly about the atmospheric circulation, atmospheric fall-out impurities, and precipitation sources, whereas chemical concentrations in strongly-melting snow during the ablation period may reflect both the related local climatic conditions and many characteristics of meltwater percolation in the snowpack. Meltwater during the ablation season causes many more impurities to percolate into the residual snow. Thus, the higher mean ionic concentrations in the June profile in this study can be explained by a greater transport of impurities by percolation. As the depth of the profile in July was lower than that in June, they received more impurities from percolating meltwater than did the June profile.

5. Conclusions

The dominant cation Ca^{2+} was far higher than the other ions. According to the ionic balances, carbonate/bicarbonate should be the dominant anion, though the dominant anion analyzed in this study was SO_4^{2-} . The mean concentrations of SO_4^{2-} and NO_3^{-} in snowpacks were higher than the mean value in a 10.3 m firn profile, which had seven complete annual layers (1997–2003), indicating the increasing anthropogenic input in this century [26]. Seasonal variations in the ionic concentrations in snowpacks are apparent and, except for Ca^{2+} concentrations, the cations show somewhat less variability than the anions. The snowpacks sampled in November, December, and January present a similar distribution of ions, showing low values in the middle part of the profile and high values in the lower part and upper part. The relatively large amplitude in variations of the ionic concentrations occurred in the snowpacks that were sampled in spring with higher ionic concentrations in the upper part of the snowpack profile. This is attributed to the variable atmospheric input with a high dust content during the period. Strong percolation of meltwater led to quick migration and redistribution

of the ions of the snowpack profiles in June and July. According to a comparison of three peak layers in the snow-firn pack, the elution sequence of the chemical species was $Ca^{2+} > SO_4^{2-} > NH_4^+ > K^+ > NO_3^- > Na^+ > Cl^- > Mg^{2+}$; since Mg^{2+} was found to be relatively immobile with respect to the percolating meltwater and the material input, it was placed at the end of the elution sequence. The potential sources for ions were identified as follows: (1) ions deposited in the winter and spring were from long-distance sources (primarily Asian dust storms) and anthropogenic sources; (2) marine sources that were transported to the area by the southwest monsoon; and (3) terrestrial materials from the local area. NO_3^- , SO_4^{2-} , and NH_4^+ were mainly supplied by wet deposition-plus-anthropogenic input, while Cl^- and Na^+ originated from marine sources. Ca^{2+} and Mg^{2+} had multiple sources and the local terrestrial source was important because of the local exposed carbonate. The chemical concentrations mainly reflect the impurities supplied by the atmospheric circulation and precipitation during the period of snow accumulation. This study is important for understanding the conditions of atmospheric deposition and environmental evolution at an alpine temperate glacier on the southeastern Tibetan Plateau.

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