



Chemical characteristics of precipitation and the indicative significance for sand dust events in the northern and southern slopes of Wushaoling Mountain, northwestern China

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Abstract: Precipitation chemistry analysis is essential to evaluate the atmospheric environmental quality and identify the sources of atmospheric pollutants. In this study, we collected a total of 480 precipitation samples at 6 sampling sites in the northern and southern slopes of Wushaoling Mountain from May 2013 to July 2014 to analyze the chemical characteristics of precipitation and to identify the main sources of ions in precipitation. Furthermore, we also explored the indicative significance for sand dust events in the northern and southern slopes of Wushaoling Mountain based on the precipitation chemistry analysis. During the sampling period (from May 2013 to July 2014), the pH values, EC (electrical conductivity) values and concentrations of cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ and NH_4^+) and anions (SO_4^{2-} , NO_3^- , Cl^- , NO_2^- and F^-) in precipitation were different in the northern and southern slopes at daily and seasonal time scales, with most of the values being higher in the northern slope than in the southern slope. The chemical type of precipitation in the southern and northern slopes was the same, i.e., SO_4^{2-} - Ca^{2+} - NO_3^- - Na^+ . The concentrations of ions in precipitation were mainly controlled by terrigenous material and anthropogenic activities (with an exception of Cl^-). The concentration of Cl^- in precipitation was mainly controlled by the sea salt fraction. The concentrations of Na^+ and Cl^- showed an increasing trend after the occurrence of sand dust events both in the northern and southern slopes. In addition, after the occurrence of sand dust events, the concentrations of K^+ , Mg^{2+} , SO_4^{2-} , NO_3^- and Ca^{2+} showed an increasing trend in the southern slope and a decreasing trend in the northern slope. It is our hope that the results may be helpful to further understand the atmospheric pollution caused by sand dust events in the Wushaoling Mountain and can also provide a scientific basis for the effective prevention of atmospheric pollution.

Keywords: precipitation chemistry; source assessment; sand dust event; Wushaoling Mountain

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1 Introduction

Precipitation chemistry is one of the foci in the researches of atmospheric science and geography (Shrestha et al., 2002; Zhang et al., 2003a, b; Mählknecht et al., 2004; Laouali et al., 2012). Precipitation chemistry analysis can evaluate the atmospheric environmental quality, reveal the acidification mechanism of precipitation, and identify the sources of atmospheric pollutants (Al-khashman, 2005; Laouali et al., 2012; Li and Morrill, 2015; Li et al., 2016, 2017a, b). In addition, precipitation chemistry analysis has some indicative significance of sand dust events (Li et al., 2017b). Water-soluble ionic components in precipitation are the combined results of natural processes and anthropogenic activities (Al-Khashman, 2005; Eneroth et al., 2007; Li et al., 2009; Laouali et al., 2012; Vet et al., 2014). The sources of these ionic components in precipitation include anthropogenic activities (combustion of fossil fuels, industrial emissions and agricultural activities), terrigenous material (including sand dust), and sea salt aerosol (Li et al., 2011; Li et al., 2012; Ma et al., 2013; Itahashi et al., 2014).

In China, the contradiction between economic growth and environmental protection is becoming increasingly acute, with the continuous development of the industrialization and urbanization processes, especially in the central and western regions (Xu et al., 2009; Li et al., 2011; Li and Morrill, 2015). Many regions in China are faced with atmospheric environmental problems such as fog haze, acid rain, extreme weather and so on (Li and Morrill, 2015; Li et al., 2016). Due to the effects of global warming, precipitation patterns in the interior region of China and the influence of the monsoon circulation have changed significantly, further leading to the variations in the chemical characteristics of precipitation (Zhu et al., 2010; Laouali et al., 2012).

Wushaoling Mountain is one of the mountain ranges in the Qilian Mountains. As a convergence zone of the Loess Plateau, Inner Mongolia Plateau and Tibetan Plateau, Wushaoling Mountain is the boundary of arid and semi-arid regions and also the boundary of monsoon and non-monsoon regions (Li et al., 2009, 2014, 2015), with the northern slope being drier than the southern slope. Chemical characteristics of precipitation in the northern and southern slopes of Wushaoling Mountain may be distinct and are worthy to be studied. However, researches on the chemical characteristics of precipitation in the Wushaoling Mountain are scarce. Study on chemical characteristics of precipitation in the Wushaoling Mountain can help to evaluate the atmospheric environmental quality and identify the sources of chemical components in precipitation in this region (Li et al., 2017a). It is of great significance to protect the ecosystem sustainability of the Qilian Mountains (Li et al., 2009; Zhu et al., 2010; Li et al., 2014, 2015, 2016).

The purposes of this study are: (1) to analyze the characteristics of pH, electrical conductivity (EC) and concentrations of major ions (including Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , SO_4^{2-} , NO_3^- , Cl^- , NO_2^- and F^-) in precipitation in the northern and southern slopes of Wushaoling Mountain; (2) to explore the relationships among these ions and identify the main sources of these ions; and (3) to discuss the indicative significance for sand dust events based on the above-mentioned precipitation chemistry analysis. The results are expected to provide scientific reference for further understanding the atmospheric environmental quality in the Wushaoling Mountain.

2 Study area and methods

2.1 Study area

Wushaoling Mountain is an important range of the Qilian Mountains, which located in the east of Hexi Corridor and the south of Wuwei City, Northwest China (102°52'00"E, 37°12'00"N). Wushaoling Mountain is the convergence zone of the Loess Plateau, Inner Mongolia Plateau and Tibetan Plateau. It has a length of 17 km from east to west and a width of 10 km from south to north. The region is characterized by a temperate semi-arid climate. Annual average temperature is 0°C, with the minimum of -30.6°C and the maximum of 28.1°C. Average annual precipitation is 401.6 mm (Yang et al., 2010, 2012). Annual average wind speed is 4.83 m/s, and the prevailing wind comes from north and southeast.

2.2 Sample collection and laboratory analysis

In this study, we collected a total of 480 precipitation samples from 6 sampling sites in the southern and northern slopes of Wushaoling Mountain, during the period from May 2013 to July 2014 (Table 1). The sampling process was manual operation. Specifically, a tin bucket (diameter of 20 cm) covered with fresh polyethylene film was placed in a height of 1.5 m above the ground at the beginning of each rainfall event. After each rainfall event, the collected rain sample was poured into a polyethylene sample bottle that cleaned with deionized water in advance. The snow samples were collected immediately after the end of the snowfall events. All samples were immediately sealed and kept in cold storage at -18°C . Anti-pollution measures were taken in the sampling process. Then, samples were transported to the laboratory of Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, and immediately stored at low temperature (-15°C). Precipitation samples were melted naturally at room temperature (about 15°C) before they were analyzed for chemical components.

The pH and electrical conductivity (EC) were measured with a PHS-3B pH meter and a DDSJ-308A conductivity meter (Shanghai Precision & Scientific Instrument Co., Ltd., China), respectively. Concentrations of cations (including Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} and NH_4^{+}) and anions (including SO_4^{2-} , NO_3^{-} , Cl^{-} , NO_2^{-} and F^{-}) were measured by DX-320 and ICS1500 (Diane Limited Company, China), respectively.

Table 1 Characteristics of sampling sites in the southern and northern slopes of Wushaoling Mountain

Wushaoling Mountain	Sampling site	Latitude	Longitude	Altitude (m)	Samples
Northern slope	Wushaoling	$37^{\circ}12'00''\text{N}$	$102^{\circ}52'00''\text{E}$	3045	51
	Heisongyi	$37^{\circ}21'29''\text{N}$	$102^{\circ}54'45''\text{E}$	2326	74
	Gulang	$37^{\circ}27'50''\text{N}$	$102^{\circ}53'21''\text{E}$	2105	83
Southern slope	Tianzhu	$36^{\circ}57'54''\text{N}$	$103^{\circ}08'17''\text{E}$	2425	40
	Jinqiangyi	$37^{\circ}08'38''\text{N}$	$102^{\circ}53'00''\text{E}$	2755	99
	Daiqian	$37^{\circ}15'19''\text{N}$	$102^{\circ}34'36''\text{E}$	3272	133

2.3 Factor analysis

In this study, we used the multivariate analytical technique to obtain the matrix of geochemical data. Specifically, we applied the factor analysis (i.e., principal component analysis (PCA)) to determine the dominant parameters by transforming a large number of correlated parameters into a small number of uncorrelated parameters (Ma et al., 2012; Li et al., 2015). We standardized the data before analysis to minimize the effects of differences in measurement units and to render the data dimensionless (Li et al., 2014). Factor analysis was explored by extracting eigenvectors and eigenvalues of the correlation matrix, and then the less important parameters were discarded (Zhu et al., 2010). Each factor was independent so that the varimax rotation could be used to constrain factors containing the greatest variability (Mahlknecht et al., 2004). In this study, we performed the algorithm of factor analysis with SPSS 22.0 software.

2.4 Enrichment factor analysis and source contribution analysis

We used the enrichment factor method to calculate the enrichment factor (degree of enrichment) of the interested ion in the objective substance with respect to the reference ion in the reference substance, which can be used to identify the sources of the interested ion (Ren et al., 2012). There are no active volcanoes around the Wushaoling Mountain, so the contribution of volcanic dust can be ignored. Therefore, it is suitable to apply the enrichment factor method in the study area. This method was firstly proposed by Keene et al. (1986). Subsequently, Xiao et al. (1993) summed up the following reference ions of ocean: (1) Na^{+} as a reference ion of ocean when $[\text{Cl}^{-}/\text{Na}^{+}]_{\text{precipitation}} \geq 1.165[\text{Cl}^{-}/\text{Na}^{+}]_{\text{ocean}}$ and $[\text{Mg}^{2+}/\text{Na}^{+}]_{\text{precipitation}} \geq 0.227[\text{Mg}^{2+}/\text{Na}^{+}]_{\text{ocean}}$; (2) Cl^{-} as a reference ion of ocean when $[\text{Na}^{+}/\text{Cl}^{-}]_{\text{precipitation}} \geq 0.859[\text{Na}^{+}/\text{Cl}^{-}]_{\text{ocean}}$ and $[\text{Mg}^{2+}/\text{Cl}^{-}]_{\text{precipitation}} \geq 0.195[\text{Mg}^{2+}/\text{Cl}^{-}]_{\text{ocean}}$; and (3) Mg^{2+} as a reference ion of ocean when

$[\text{Na}^+/\text{Mg}^{2+}]_{\text{precipitation}} \geq 4.403[\text{Na}^+/\text{Mg}^{2+}]_{\text{ocean}}$ and $[\text{Cl}^-/\text{Mg}^{2+}]_{\text{precipitation}} \geq 5.126[\text{Cl}^-/\text{Mg}^{2+}]_{\text{ocean}}$.

In this study, we determined the reference ion of ocean according to the above-mentioned rules, and selected Ca^{2+} as the reference ion of crust according to the study of Taylor (1964). The enrichment factor of the interested ion in precipitation with respect to the reference ion of crust (EF_{crust}) and the enrichment factor of the interested ion in precipitation with respect to the reference ion of ocean (EF_{ocean}) were calculated as follows (Okay et al., 2002; Ren et al., 2012):

$$EF_{\text{crust}} = [X/\text{Ca}^{2+}]_{\text{precipitation}} / [X/\text{Ca}^{2+}]_{\text{crust}}, \quad (1)$$

$$EF_{\text{ocean}} = [X/N]_{\text{precipitation}} / [X/N]_{\text{ocean}}, \quad (2)$$

where X is the concentration of the interested ion in precipitation (mol/L), and N is the concentration of the reference ion in ocean (mol/L). In this study, the value of $[X/\text{Ca}^{2+}]_{\text{crust}}$ was referred from the crustal data in the study of Taylor (1964), and the value of $[X/N]_{\text{ocean}}$ was referred from the ocean data in the study of Keene et al. (1986). Generally speaking, $EF \leq 1$ represents that the interested ion in precipitation is diluted, while $EF > 1$ represents that the interested ion in precipitation is enriched.

The sources of ions in precipitation include anthropogenic activities, terrigenous material, and sea salt aerosol. We therefore calculated the sea salt fraction (SSF), crust fraction (CF) and anthropogenic fraction (AF) to identify the sources of ions in precipitation. They were calculated by the following equations (Keene et al., 1986; Li et al., 2015):

$$\text{SSF} (\%) = 100 \times [X/N]_{\text{ocean}} / [X/N]_{\text{precipitation}}, \quad (3)$$

$$\text{CF} (\%) = 100 \times [X/\text{Ca}^{2+}]_{\text{crust}} / [X/\text{Ca}^{2+}]_{\text{precipitation}}, \quad (4)$$

$$\text{AF} (\%) = 100\% - \text{SSF} - \text{CF}. \quad (5)$$

3 Results

3.1 Variations in pH values of precipitation

During the sampling period (i.e., from May 2013 to July 2014), the pH values of precipitation in the southern and northern slopes of Wushaoling Mountain almost showed the same variation range, with the average value in the northern slope being slightly higher than that in the southern slope. Specifically, pH values of precipitation ranged from 6.81 to 8.68 in the southern slope (average of 7.50) and from 6.66 to 8.54 in the northern slope (average of 7.55). The pH values of precipitation in the northern and southern slopes were almost alkaline. Seasonal variations in pH values of precipitation in the southern and northern slopes of Wushaoling Mountain are shown in Figure 1. It can be seen that the average pH in precipitation was highest in summer both in the southern and northern slopes.

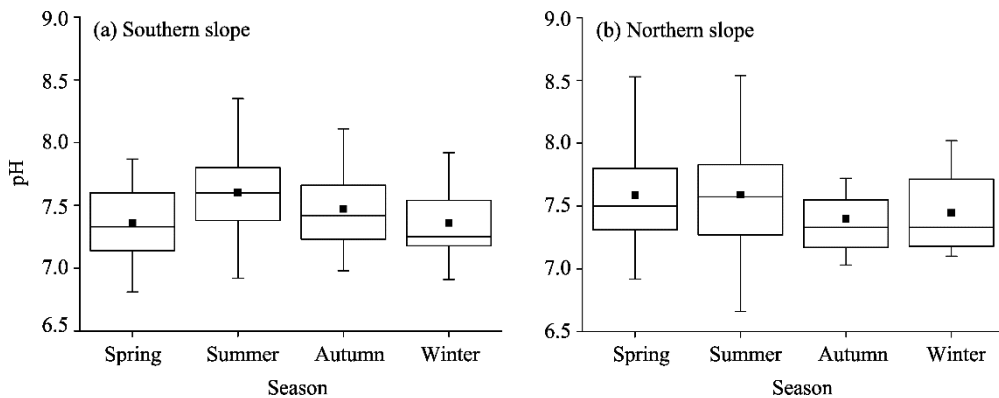


Fig. 1 Seasonal variations in pH values of precipitation in the southern (a) and northern (b) slopes of Wushaoling Mountain. The median of the data is presented by the line inside of the rectangle and “whiskers” above and below the box display the locations of the maximum and minimum values, respectively. The black square inside of the rectangle represents the outlier.

3.2 Variations in EC values of precipitation

In the southern slope of Wushaoling Mountain, the EC values of precipitation ranged from 13.15 to 1086.00 $\mu\text{S}/\text{cm}$, with a mean of 156.07 $\mu\text{S}/\text{cm}$; while in the northern slope, the values ranged from 17.28 to 971.50 $\mu\text{S}/\text{cm}$, with a mean of 179.60 $\mu\text{S}/\text{cm}$ (Fig. 2). In the southern slope, the highest EC value was observed on 1 May, 2014 and the lowest value appeared on 15 September, 2013. In the northern slope, the highest EC value was observed on 24 April, 2014 and the lowest value appeared on 11 August, 2013. At seasonal scale, the EC values of precipitation in the southern slope were all lower than those in the northern slope. As shown in Figure 2c, the EC values of precipitation were higher in spring and winter than in summer and autumn. This may be due to the frequent sand dust events in spring and winter.

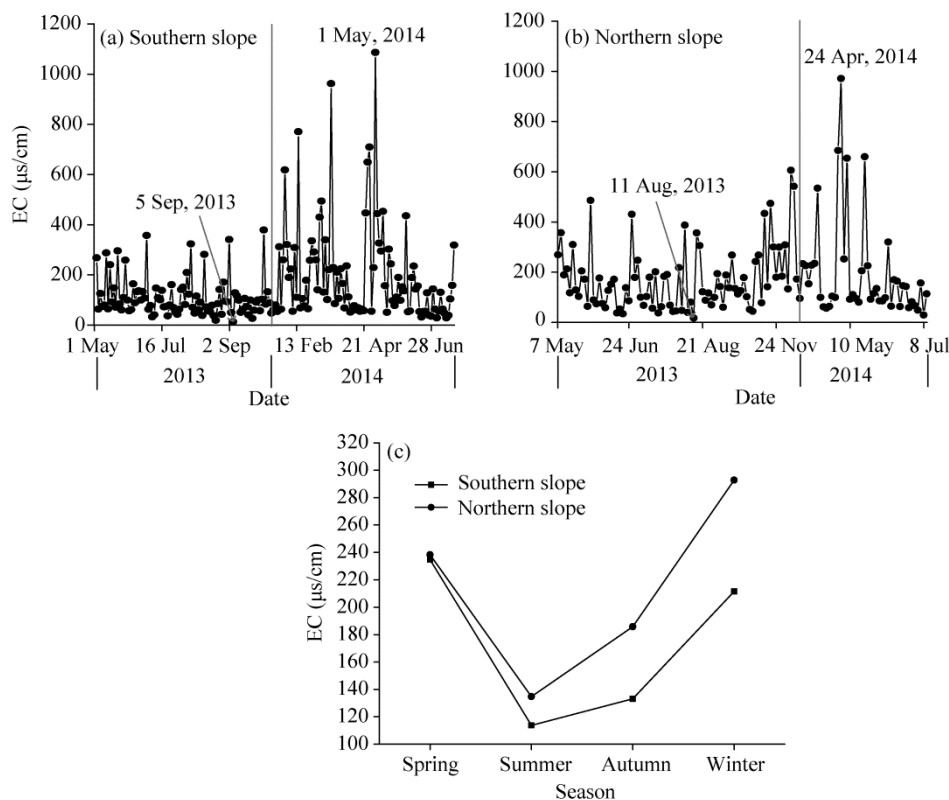


Fig. 2 Variations of electrical conductivity (EC) in precipitation in the northern and southern slopes of Wushaoling Mountain from May 2013 to July 2014 at daily (a, b) and seasonal (c) scales

3.3 Variations in ion concentrations of precipitation

Concentrations of ions in precipitation in the northern and southern slopes of Wushaoling Mountain are shown in Table 2. It can be seen that concentrations of Mg^{2+} , Ca^{2+} , NH_4^+ , F^- , NO_3^- , and SO_4^{2-} were significant between the northern and southern slopes, while there was no significant difference in concentrations of Na^+ , K^+ , Cl^- , and NO_2^- between the northern and southern slopes.

In the southern slope of Wushaoling Mountain, Ca^{2+} and Na^+ dominated the cations of precipitation (accounting for 83.58% of the total cation composition), while SO_4^{2-} and NO_3^- dominated the anions (accounting for 83.78% of the total anion composition) (Fig. 3). The chemical type of precipitation in the southern slope was $\text{SO}_4^{2-}\text{-Ca}^{2+}\text{-NO}_3^-\text{-Na}^+$, with the four ions accounting for 83.69% of the total ion concentration. In the northern slope of Wushaoling Mountain, also the Ca^{2+} and Na^+ dominated the cations (accounting for 73.18% of the total cation composition), and SO_4^{2-} and NO_3^- dominated the anions (accounting for 83.82% of the total anion composition). The chemical type of precipitation in the northern slope was $\text{SO}_4^{2-}\text{-Ca}^{2+}\text{-NO}_3^-\text{-Na}^+$,

with the four ions accounting for 79.77% of the total ion concentration. In addition, the percentage of individual ion concentration in precipitation was in the order of $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+} > \text{NH}_4^+ > \text{F}^- > \text{NO}_2^-$ in the southern slope, and in the order of $\text{SO}_4^{2-} > \text{Ca}^{2+} > \text{NO}_3^- > \text{Cl}^- > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{NH}_4^+ > \text{NO}_2^- > \text{F}^-$ in the northern slope. It can be seen that the order of the percentage of individual ion concentration in precipitation was basically the same in the southern and northern slopes.

Table 2 Concentrations of ions in precipitation in the northern and southern slopes of Wushaoling Mountain

Wushaoling Mountain	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+
	($\mu\text{eq/L}$)				
Southern slope	3.50 ± 0.51^a	1.70 ± 0.18^a	1.66 ± 0.15^A	17.78 ± 1.34^A	0.82 ± 0.06^A
Northern slope	4.69 ± 0.78^a	1.95 ± 0.31^a	2.74 ± 0.34^B	12.26 ± 1.06^B	1.52 ± 0.15^B
Wushaoling Mountain	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
	($\mu\text{eq/L}$)				
Southern slope	0.17 ± 0.02^a	4.74 ± 0.89^a	0.14 ± 0.03^a	10.40 ± 0.90^a	15.69 ± 1.83^a
Northern slope	0.11 ± 0.01^b	5.82 ± 0.95^a	0.15 ± 0.06^a	7.69 ± 0.82^b	23.82 ± 2.83^b

Note: Mean \pm SE. Different uppercase letters with a column indicate significant difference of ion concentration in precipitation between the southern and northern slopes at $P < 0.01$ level; while different lowercase letters with a column indicate significant difference of ion concentration in precipitation between the southern and northern slopes at $P < 0.05$ level.

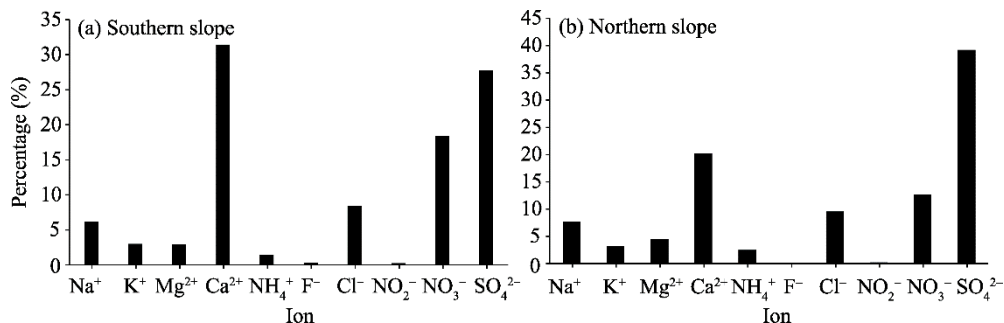


Fig. 3 Percentage of individual ion concentration in precipitation in the northern and southern slopes of Wushaoling Mountain

At seasonal scale, the total ion concentration in precipitation was in the order of spring > winter > autumn > summer in the southern slope of Wushaoling Mountain (Fig. 4a) and in the order of winter > spring > autumn > summer in the northern slope (Fig. 4b). In the southern slope, the concentration of Ca^{2+} in precipitation was higher in spring than in winter, and higher in summer than in autumn. In the northern slope, the concentration of Ca^{2+} in precipitation was also higher in spring than in winter, and higher in summer than in autumn. The concentration of SO_4^{2-} was highest in winter and spring in the northern slope and southern slope, respectively. The seasonal variation of NO_3^- in precipitation in the northern and southern slopes exhibited the same order, that is, winter > spring > autumn > summer. The concentration of Na^+ in precipitation showed the same seasonal variation in the northern and southern slopes. The seasonal variation of Cl^- in precipitation was in the order of winter > spring > autumn > summer in the northern slope, and in the order of spring > winter > autumn > summer in the southern slope.

3.4 Relationships of ions in precipitation

Relationships of ions in precipitation in the southern and northern slopes of Wushaoling Mountain are shown in Tables 3 and 4, respectively. The SO_4^{2-} in precipitation showed significant correlations with Na^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- and NO_3^- in precipitation both in the southern and northern slopes. In the southern slope, the NO_3^- in precipitation showed significant correlations with Na^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- and Cl^- in precipitation; while in the northern slope, the NO_3^- in precipitation was significantly correlated with Na^+ , K^+ , F^- and Cl^- in precipitation. The Cl^- in

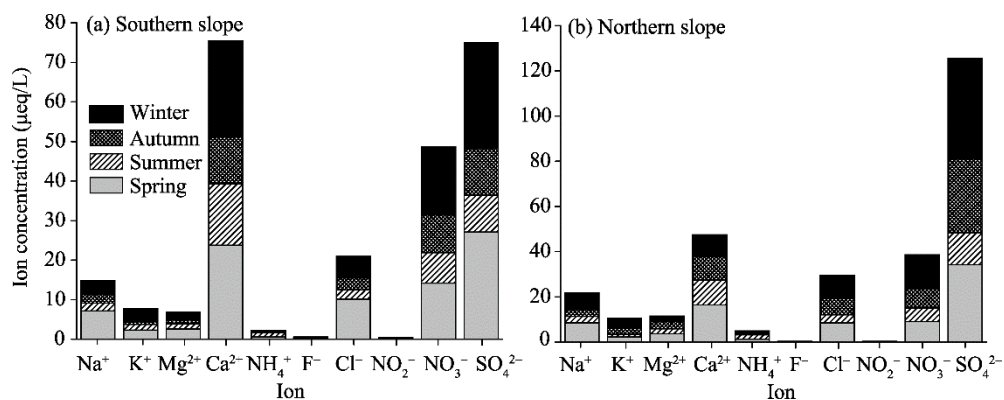


Fig. 4 Seasonal variations of ion concentrations in precipitation in the southern (a) and northern (b) slopes of Wushaoling Mountain

precipitation was significantly correlated with Na^+ , K^+ , Mg^{2+} , Ca^{2+} and F^- in precipitation both in the southern and northern slopes of Wushaoling Mountain (Tables 3 and 4). The NH_4^+ in precipitation showed significant correlations with SO_4^{2-} and NO_3^- in precipitation in the southern slope, indicating that NH_4^+ was the major neutralizing ion for SO_4^{2-} and NO_3^- . By comparing the correlation coefficients among all ions in precipitation between the southern slope and the northern slope, we found that the correlation coefficients among Na^+ , K^+ , Mg^{2+} , Ca^{2+} and NO_3^- in the southern slope were higher than those in the northern slope, while the coefficient between F^- and Cl^- in the northern slope was higher than that in the southern slope.

4 Discussion

4.1 Sources of ions in precipitation

Generally speaking, the ion concentrations of precipitation were higher in the northern slope than in the southern slope of Wushaoling Mountain. This may be due to that the northern slope is near to the sand dust sources, especially near to the deserts. Furthermore, there are many cement factories distributed in the northern slope, leading to the increase in the ion concentrations in precipitation. At seasonal scale, the ion concentrations of precipitation were relatively high in winter and spring both in the southern and northern slopes. This may be related to the low precipitation, high wind speed, and frequent sand dust events in these two seasons. Sand dust events can increase the terrigenous material in the atmosphere (Li et al., 2017b), inevitably resulting in the increase of ion concentrations in precipitation. By contrast, the ion concentrations of precipitation were relatively low in summer and autumn, which may be related to the high precipitation amount. Specifically, the influence of dilution effect from precipitation on the ion concentrations was more obvious in summer and autumn, leading to the low ion concentrations.

Generally speaking, the SO_4^{2-} was mainly from the local sources. On the one hand, it was from the contribution of weathering effect of the sulphate minerals, which related to the enrichment of CaSO_4 and MgSO_4 . On the other hand, it was from the SO_2 created by the industrial production and anthropogenic activities. The Ca^{2+} and Mg^{2+} are two important crustal material components, reflecting that the important influences of MgSO_4 and CaSO_4 are from the local source particles (Al-khashman, 2005; Eneroth et al., 2007; Li et al., 2014). The NO_3^- was mainly from the pollutant emissions of anthropogenic activities in the southern slope, and from the oil consumption and pollutant emissions of anthropogenic activities in the northern slope. The average ratio of Na^+ concentration to Cl^- concentration in precipitation was 0.73 in the southern slope and 0.81 in the northern slope (Table 2), being lower than the average ratio of Na^+ concentration to Cl^- concentration in seawater (0.86) (Al-khashman, 2005; Eneroth et al., 2007). This suggested that the sources of Cl^- in precipitation were complex, and the Cl^- may probably come from the ocean sources, local sources and anthropogenic activities. The ratio of K^+

Table 3 Pearson correlation analysis of ions in precipitation in the southern slope of Wushaoling Mountain

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻
Na ⁺	1.000									
K ⁺	0.538**	1.000								
Mg ²⁺	0.743**	0.471	1.000							
Ca ²⁺	0.693**	0.682**	0.615**	1.000						
NH ₄ ⁺	-0.157	-0.163	-0.169	-0.198	1.000					
F ⁻	0.306**	0.319**	0.316**	0.453**	0.005	1.000				
Cl ⁻	0.737**	0.392**	0.370**	0.463**	-0.032	0.339**	1.000			
NO ₂ ⁻	0.081	0.268**	0.086	0.102	0.016	0.114	0.108	1.000		
NO ₃ ⁻	0.483**	0.579**	0.356**	0.576**	-0.210**	0.452**	0.411**	0.038	1.000	
SO ₄ ²⁻	0.665**	0.555**	0.538**	0.698**	-0.201**	0.544**	0.530**	0.041	0.764**	1.000

Note: ** means correlation is significant at $P < 0.01$ level (2-tailed).

Table 4 Pearson correlation analysis of ions in precipitation in the northern slope of Wushaoling Mountain

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻
Na ⁺	1.000									
K ⁺	0.549**	1.000								
Mg ²⁺	0.579**	0.256**	1.000							
Ca ²⁺	0.412**	0.258**	0.292**	1.000						
NH ₄ ⁺	-0.173	-0.065	-0.239	-0.119	1.000					
F ⁻	0.276**	0.366**	0.187	0.292**	0.152	1.000				
Cl ⁻	0.690**	0.475**	0.361**	0.319**	-0.104	0.576**	1.000			
NO ₂ ⁻	0.153	0.228	0.038	0.159	-0.046	0.095	0.101	1.000		
NO ₃ ⁻	0.428**	0.411**	0.226	0.145	-0.142	0.345**	0.510**	0.028	1.000	
SO ₄ ²⁻	0.630**	0.452**	0.343**	0.324**	-0.021	0.671**	0.896**	0.059	0.526**	1.000

Note: ** means correlation is significant at $P < 0.01$ level (2-tailed).

concentration to Cl⁻ concentration in precipitation was 0.36 in the southern slope and 0.34 in the northern slope (Table 2), being higher than the ratio of K⁺ concentration to Cl⁻ concentration in seawater (0.061). This suggested that the contribution of ocean to K⁺ can be ignored. By contrast, local sources and anthropogenic activities may play an important role in the concentration of K⁺.

In the southern slope of Wushaoling Mountain, the first three PC (principal component) factors explained 66.67% of the total variance of precipitation chemistry (Table 5). Specifically, the first PC factor explained 44.24% of the total variance of precipitation chemistry, and this factor had high loading eigenvalues of all ions (with exceptions of NH₄⁺ and NO₂⁻). This suggested that ions in precipitation were mainly from the local sources. The second PC factor explained 11.90% of the total variance of precipitation chemistry, and this factor had high loading eigenvalue of NO₂⁻. This indicated that industrial emissions, municipal waste incineration and automobile exhaust also contributed to the chemical characteristics of precipitation. The third PC factor explained 10.53% of the total variance of precipitation chemistry, and this factor had high loading eigenvalues of NH₄⁺ and F⁻. This reflected the contribution of industrial and agricultural production, and organic decomposition on the chemical characteristics of precipitation.

In the northern slope of Wushaoling Mountain, the first three PC factors explained 64.83% of the total variance of precipitation chemistry (Table 5). The first PC factor explained 40.78% of the total variance of precipitation chemistry, and this factor had high loading eigenvalues of all ions (with exceptions of NH₄⁺ and NO₂⁻). This indicated that ions in precipitation were mainly from local sources. The second PC factor explained 13.07% of the total variance of precipitation chemistry, and this factor had high loading eigenvalue of NH₄⁺ and F⁻. This suggested the

contribution of industrial and agricultural production, and organic decomposition on the chemical characteristics of precipitation. The third PC factor explained 10.98% of the total variance of precipitation chemistry, and this factor had high loading eigenvalue of NO_2^- . This reflected the contribution of waste gas emissions from industrial production, municipal waste incineration and automobile exhaust.

Table 5 Eigenvalues and variances of the first three PC (principal component) factors for ions in precipitation in the southern and northern slopes of Wushaoling Mountain

Eigenvalue/Variance	Southern slope			Northern slope		
	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3
Na^+	0.829	0.360	−0.041	0.824	−0.257	−0.020
K^+	0.776	0.120	−0.199	0.640	−0.126	0.351
Mg^{2+}	0.743	0.127	−0.274	0.608	−0.404	−0.185
Ca^{2+}	0.869	−0.008	−0.149	0.568	−0.127	0.229
NH_4^+	−0.256	0.368	0.698	−0.164	0.755	0.237
F^-	0.540	−0.248	0.533	0.617	0.562	0.072
Cl^-	0.577	0.414	0.278	0.875	0.184	−0.135
NO_2^-	0.227	0.554	−0.039	0.204	−0.180	0.847
NO_3^-	0.697	−0.444	0.142	0.586	0.001	−0.255
SO_4^{2-}	0.774	−0.395	0.209	0.860	0.306	−0.159
Percentage of variance (%)	44.24	11.90	10.53	40.78	13.07	10.98
Cumulative percentage of variance (%)	44.24	56.14	66.67	40.78	53.85	64.83

We used the enrichment factor method to identify the sources of ions in precipitation in the Wushaoling Mountain. It should be noted again that the sources of ions in precipitation include anthropogenic activities, terrigenous material, and sea salt aerosol (Al-khashman, 2005; Li et al., 2014, 2015, 2016; Guo et al., 2015). We calculated the $[\text{Cl}^-/\text{Na}^+]_{\text{precipitation}}=1.35[\text{Cl}^-/\text{Na}^+]_{\text{ocean}}$ and $[\text{Mg}^{2+}/\text{Na}^+]_{\text{precipitation}}=0.47[\text{Cl}^-/\text{Na}^+]_{\text{ocean}}$ for the southern slope, and the $[\text{Cl}^-/\text{Na}^+]_{\text{precipitation}}=1.24[\text{Cl}^-/\text{Na}^+]_{\text{ocean}}$ and $[\text{Mg}^{2+}/\text{Na}^+]_{\text{precipitation}}=0.58[\text{Cl}^-/\text{Na}^+]_{\text{ocean}}$ in the northern slope, suggesting that Na^+ was the reference ion of ocean (Xiao et al., 1993).

The enrichment factors of ions in precipitation in the southern and northern slopes of Wushaoling Mountain are shown in Table 6. The EF_{crust} values of Na^+ were generally lower than 1 both in the southern and northern slopes, indicating that Na^+ was derived from the crust. The EF_{crust} values of K^+ were much lower than 1 while the EF_{ocean} values of K^+ were much higher than 1, which suggested that K^+ was mainly derived from the crust. The EF_{crust} values of Mg^{2+} were lower than 1 while the EF_{ocean} values of Mg^{2+} were higher than 1 in the two slopes, indicating that Mg^{2+} was mainly from the crust. The EF_{crust} values of Cl^- ranged from 46.83 to 138.05 in the southern slope and from 108.93 to 326.84 in the northern slope; and, only in autumn in the northern slope, the EF_{ocean} value of Cl^- was higher than 1. This suggested that ocean was the main source for Cl^- . The EF_{crust} values of NO_3^- were higher than 233.77 and the EF_{ocean} values of NO_3^- were higher than 717.07 in the southern and northern slopes, indicating that ocean and crust almost exhibited no contribution to NO_3^- , and the main source of NO_3^- was anthropogenic activities. In addition, SO_4^{2-} was also mainly from anthropogenic activities. The EF_{ocean} values of Ca^{2+} ranged from 89.66 to 212.01 in the southern slope and from 35.61 to 102.11 in the northern slope, suggesting that Ca^{2+} was mainly from the crust. The EF_{ocean} values of F^- were higher than 1 in the two slopes, which indicated that F^- was mainly from the crust.

In this study, we calculated the source contributions of sea salt fraction, crust fraction and anthropogenic fraction (Equations 3–5, respectively) to further determine the sources of ions in precipitation in the study area (Mahlknecht et al., 2004; Li et al., 2015). The results are shown in Table 7. The NO_3^- in precipitation was mainly from the anthropogenic activities, with contribution of 99.64% in the southern slope of Wushaoling Mountain and 99.69% in the northern slope. Only

a small part of SO_4^{2-} was contributed from the ocean fraction and crust fraction. The contributions of crust fraction and anthropogenic fraction for Mg^{2+} and K^+ in precipitation were 76.00% and 93.75% in the southern slope, and 80.35% and 93.43% in the northern slope, respectively. Similarly, the F^- in precipitation in the southern and northern slopes was mainly affected by crust and anthropogenic activities, with contributions of 87.86% and 76.18%, respectively. Different from the other ions, the Cl^- in precipitation mainly came from the sea salt fraction, with the contributions of 98.83% and 99.53% in the southern and northern slopes, respectively.

Table 6 Enrichment factors of ions in precipitation in the southern and northern slopes of Wushaoling Mountain with respect to the reference ion in the reference substance

Southern slope	Enrichment factor of ion in precipitation relative to Ca^{2+} in crust						Enrichment factor of ion in precipitation relative to Na^+ in ocean						
	Na^+	K^+	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
Spring	0.53	0.19	0.19	138.05	285.29	60.77	8.74	2.84	89.66	3.88	0.71	1342.82	15.53
Summer	0.22	0.18	0.15	46.83	233.77	31.34	19.7	5.25	212.01	10.77	0.57	2601.90	18.94
Autumn	0.32	0.14	0.17	82.30	381.94	53.22	10.04	4.10	147.28	9.97	0.69	2953.28	22.35
Winter	0.25	0.26	0.14	73.55	338.03	58.83	25.50	4.36	192.53	8.32	0.81	3416.75	32.29
Northern slope	Enrichment factor of ion in precipitation relative to Ca^{2+} in crust						Enrichment factor of ion in precipitation relative to Na^+ in ocean						
	Na^+	K^+	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
Spring	0.91	0.26	0.4	164.63	262.06	110.30	6.88	3.45	52.12	1.99	0.49	717.07	16.39
Summer	0.47	0.24	0.35	108.93	264.58	69.67	12.25	5.91	102.11	4.97	0.63	1418.42	20.28
Autumn	0.51	0.59	0.55	237.19	407.17	169.53	27.85	8.38	93.14	6.17	1.26	1990.94	45.01
Winter	1.33	0.77	0.45	326.84	712.50	239.53	13.82	2.62	35.61	3.66	0.66	1331.98	24.32

Table 7 Source contributions for different ions in precipitation in the southern and northern slopes of Wushaoling Mountain

	Source	Fraction	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
Southern slope	Ocean source	SSF (%)	0.00	6.25	24.00	0.00	12.14	98.83	0.32	4.48
	Land source	CF (%)	100.00	93.75	76.00	100.00	87.86	1.17	0.04	1.95
		AF (%)	0.00			0.00		0.00	99.64	93.57
	Source	Fraction	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
Northern slope	Ocean source	SSF (%)	0.00	6.57	19.65	0.00	23.82	99.53	0.07	3.77
	Land source	CF (%)	100.00	93.43	80.35	100.00	76.18	0.47	0.24	0.67
		AF (%)	0.00			0.00		0.00	99.69	95.56

Note: SSF, sea salt fraction; CF, crust fraction; AF, anthropogenic fraction.

4.2 Indicative significance for sand dust events

In order to study the indication of precipitation chemistry to sand dust events, we selected three typical sand dust events occurred in the Wushaoling Mountain based on the frequency of sand dust events and the temporal distribution of precipitation. Specifically, we analyzed the changes in chemical characteristics of precipitation after the occurrence of sand dust events. The first sand dust event occurred on 22 May, 2013; the second sand dust event occurred on 23 and 24 April, 2014; and the third sand dust event occurred on 30 April, 2014. It should be noted that for the three selected sand dust events, precipitation occurred after the occurrence of sand dust events.

As shown in Figure 5, Na^+ in precipitation exhibited a high concentration after the occurrence of sand dust events both in the southern and northern slopes of Wushaoling Mountain. As above-mentioned analysis, Na^+ in precipitation was mainly from the terrigenous material. Sand dust events could increase the terrigenous material in the atmosphere, leading to the increase in the concentration of Na^+ in precipitation. After the occurrence of sand dust events, the

concentrations of K^+ , Mg^{2+} , SO_4^{2-} , NO_3^- and Ca^{2+} in precipitation increased in the southern slope and decreased in the northern slope. There may be two possible reasons. On the one hand, these ions were mainly from the terrigenous material and anthropogenic activities. On the other hand, a large number of sand dusts were blown to the southern slope when the sand dust events occurred, thereby increasing the ion concentrations in precipitation in the southern slope and decreasing the ion concentrations in the northern slope. The concentration of Cl^- increased after the occurrence of sand dust events both in the southern and northern slopes, indicating that the sands and dusts contained a high concentration of NaCl .

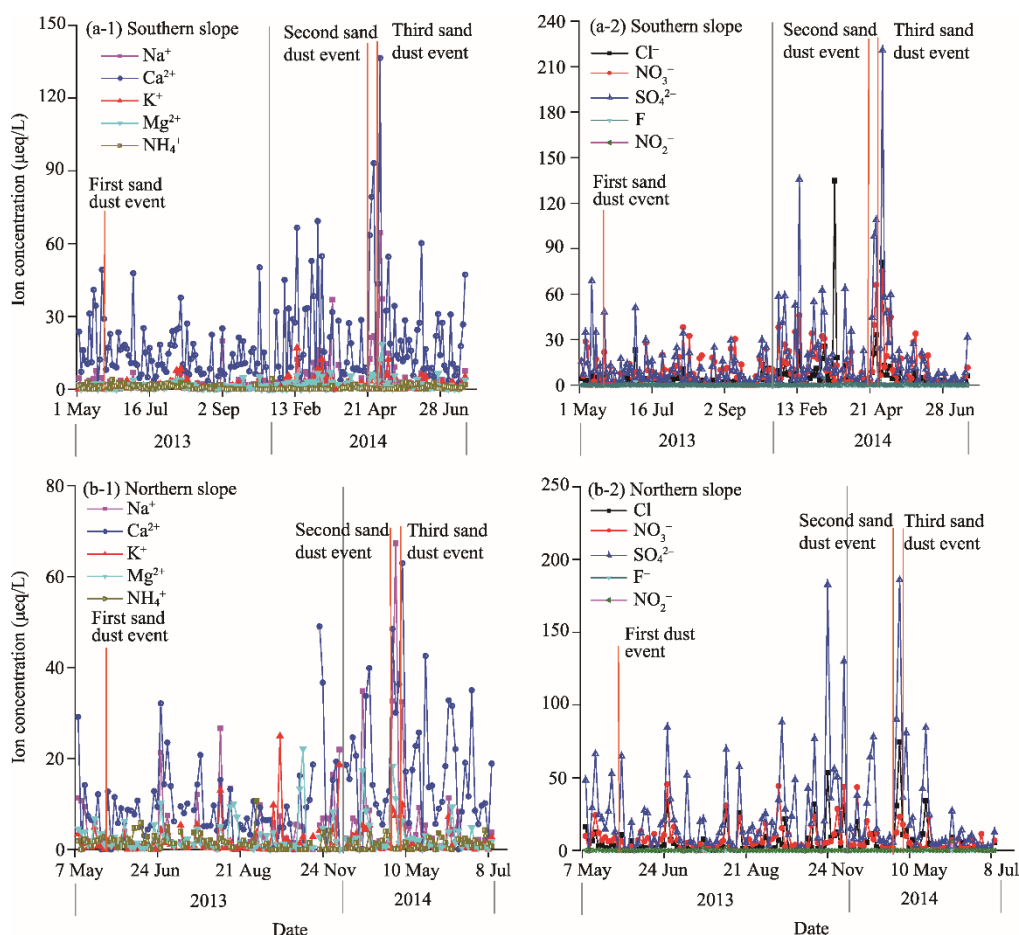


Fig. 5 Concentrations of ions in precipitation in the southern and northern slopes of Wushaoling Mountain. It should be noted that the first sand dust event occurred on 22 May, 2013 (orange line); the second sand dust event occurred on 23 and 24 April, 2014; and the third sand dust event occurred on 30 April, 2014.

5 Conclusions

During the sampling period (i.e., from May 2013 to July 2014), the pH values of precipitation in the southern and northern slopes of Wushaoling Mountain exhibited the same variation range, with the average value in the northern slope being slightly higher than that in the southern slope. The EC values of precipitation in the northern slope were higher than those in the southern slope. Concentrations of Mg^{2+} , Ca^{2+} , NH_4^+ , F^- , NO_3^- , and SO_4^{2-} showed significant difference between the northern and southern slopes. The chemical type of precipitation was similar in the southern and northern slopes, i.e., SO_4^{2-} - Ca^{2+} - NO_3^- - Na^+ . The land sources (including terrigenous material and anthropogenic activities) played an important role in determining the ion concentrations of precipitation both in the southern and northern slopes (with an exception of Cl^-). The Cl^- in

precipitation mainly came from the sea salt fraction. After the occurrence of sand dust events, the concentration of Na^+ in precipitation increased both in the southern and northern slopes. Furthermore, the concentrations of K^+ , Mg^{2+} , SO_4^{2-} , NO_3^- and Ca^{2+} in precipitation in the southern slope increased, while the concentrations decreased in the northern slope. This results are helpful to further understand the atmospheric pollution caused by sand dust events in the Wushaoling Mountain and can also provide a scientific basis for the effective prevention of atmospheric pollution in this region.

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