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Full Text

Preamble

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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 atmospheric environmental quality and identify the sources of atmospheric pollutants. In this study, we collected a total of 480 precipitation samples at six 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 identify the main sources of ions. Furthermore, we explored the indicative significance for sand dust events in the northern and southern slopes of Wushaoling Mountain based on precipitation chemistry analysis.

During the sampling period (May 2013 to July 2014), the pH values, EC (electrical conductivity) values, and concentrations of cations (Ca^{2} , Mg^{2} , Na , K and NH) and anions (SO^{2} , NO , Cl , and F) in precipitation differed between the northern and southern slopes at daily and seasonal time scales, with most values being higher in the northern slope than in the southern slope. The chemical type of precipitation was the same in the southern and northern slopes, i.e., SO^{2}-Na . The concentrations of ions in precipitation were mainly controlled by terrigenous material and anthropogenic activities (with the exception of Cl). The concentration of Cl in precipitation was primarily controlled by sea salt fraction. The concentrations of Na and Cl showed an increasing trend after the occurrence of sand dust events in both the northern and southern slopes. In addition, after sand dust events, the concentrations of K , Mg^{2} , SO^{2} and Ca^{2} showed an increasing trend in the southern slope and a decreasing trend in the northern slope. We hope these results will help further understand atmospheric pollution caused by sand dust events in Wushaoling Mountain and provide a scientific basis for effective prevention of atmospheric pollution.

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

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1 Introduction

Precipitation chemistry is a focal point in atmospheric science and geography research (Shrestha et al., 2002; Zhang et al., 2003a, b; Mahlknecht et al., 2004; Laouali et al., 2012). Precipitation chemistry analysis can evaluate 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 indicative significance for 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 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 continuous industrialization and urbanization, especially in central and western regions (Xu et al., 2009; Li et al., 2011; Li and Morrill, 2015). Many regions face atmospheric environmental problems such as fog, haze, acid rain, and extreme weather (Li and Morrill, 2015; Li et al., 2016). Due to global warming, precipitation patterns in China’ s interior and the influence of monsoon circulation have changed significantly, further leading to 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 forms the boundary between arid and semi-arid regions and between 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 may be distinct and warrant investigation. However, research on precipitation chemistry in Wushaoling Mountain is scarce. Studying precipitation chemistry can help evaluate atmospheric environmental quality and identify sources of chemical components in this region (Li et al., 2017a), which is significant for protecting ecosystem sustainability in 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 characteristics of pH, electrical conductivity (EC), and concentrations of major ions (including Ca^2 , Mg^2 , Na , K , NH , SO^2 , NO , and F) in precipitation in the northern and southern slopes of Wushaoling Mountain; (2) to explore relationships among these ions and identify their main sources; and (3) to discuss the indicative significance for sand dust events based on precipitation chemistry analysis. The results are expected to provide scientific reference for further understanding atmospheric environmental quality in Wushaoling Mountain.

2.1 Study Area

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

2.2 Sample Collection and Laboratory Analysis

In this study, we collected a total of 480 precipitation samples from six sampling sites in the southern and northern slopes of Wushaoling Mountain from May 2013 to July 2014 (Table 1). Sampling was conducted manually. Specifically, a tin bucket (20 cm diameter) covered with fresh polyethylene film was placed 1.5 m above ground at the beginning of each rainfall event. After each event, collected rain samples were transferred to polyethylene bottles pre-cleaned with deionized water. Snow samples were collected immediately after snowfall events ended. All samples were immediately sealed and stored at -18°C. Anti-pollution measures were taken during sampling. Samples were transported to the laboratory of Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, and stored at low temperature (-15°C). Precipitation samples were melted naturally at room temperature (approximately 15°C) before chemical analysis.

pH and electrical conductivity (EC) were measured using a PHS-3B pH meter and DDSJ-308A conductivity meter (Shanghai Precision & Scientific Instrument Co., Ltd., China), respectively. Concentrations of cations (Ca^{2} , Mg^{2} , Na , K , and NH) and anions (SO ^{2} , NO , Cl , NO , 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°12 00 N	102°52 00 E		

Wushaoling Mountain	Sampling site	Latitude	Longitude	Altitude (m)	Samples
Southern slope	Heisongyi	37°21 29 N	102°54 45 E		
	Gulang	37°27 50 N	102°53 21 E		
	Tianzhu	36°57 54 N	103°08 17 E		
	Jinqiangyi	37°08 38 N	102°53 00 E		
	Daiqian	37°15 19 N	102°34 36 E		

2.3 Factor Analysis

This study employed multivariate analytical techniques to obtain the geochemical data matrix. Specifically, we applied factor analysis (principal component analysis, PCA) to determine dominant parameters by transforming numerous correlated parameters into a smaller set of uncorrelated parameters (Ma et al., 2012; Li et al., 2015). Data were standardized before analysis to minimize effects of measurement unit differences and render data dimensionless (Li et al., 2014). Factor analysis was performed by extracting eigenvectors and eigenvalues from the correlation matrix, after which less important parameters were discarded (Zhu et al., 2010). Each factor was independent, allowing varimax rotation to constrain factors containing the greatest variability (Mahlknecht et al., 2004). We performed factor analysis using SPSS 22.0 software.

2.4 Enrichment Factor Analysis and Source Contribution Analysis

We used the enrichment factor method to calculate the degree of enrichment of target ions in precipitation relative to reference ions in reference substances, which helps identify ion sources (Ren et al., 2012). No active volcanoes exist near Wushaoling Mountain, so volcanic dust contributions can be ignored, making the enrichment factor method suitable. This method was first proposed by Keene et al. (1986). Subsequently, Xiao et al. (1993) summarized the following reference ions for oceanic sources: (1) Na as ocean reference ion when [Cl /Na]precipitation 1.165[Cl /Na]ocean and [Mg^2 /Na]precipitation 0.227[Mg^2 /Na]ocean; (2) Cl as reference ion when [Mg^2 /Cl]precipitation 0.195[Mg^2 /Cl]ocean; and (3) Mg^2 as reference ion when [Na /Cl]precipitation 0.859[Na /Cl]ocean, [Na /Mg^2]precipitation 4.403[Na /Mg^2]ocean, and [Cl /Mg^2]precipitation 5.126[Cl /Mg^2]ocean.

In this study, we determined oceanic reference ions using these rules and selected Ca^2 as the crustal reference ion based on Taylor (1964). Enrichment factors relative to crust (EFcrust) and ocean (EFocean) were calculated as follows (Okay et al., 2002; Ren et al., 2012):

$$EF_{crust} = \frac{[X/Ca^{2+}]_{precipitation}}{[X/Ca^{2+}]_{crust}}$$

$$EF_{ocean} = \frac{[X/N]_{precipitation}}{[X/N]_{ocean}}$$

where X is the concentration of the target ion in precipitation (mol/L), and N is the concentration of the reference ion in ocean (mol/L). In this study, [X/Ca²]crust values were taken from crustal data in Taylor (1964), and [X/N]ocean values from oceanic data in Keene et al. (1986). Generally, EF 1 indicates dilution of the target ion in precipitation, while EF > 1 indicates enrichment.

Precipitation ion sources include anthropogenic activities, terrigenous material, and sea salt aerosol. We therefore calculated sea salt fraction (SSF), crust fraction (CF), and anthropogenic fraction (AF) to identify ion sources using the following equations (Keene et al., 1986; Li et al., 2015):

$$SSF(\%) = 100 \times \frac{[X/N]_{ocean}}{[X/N]_{precipitation}}$$

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

$$AF(\%) = 100\% - SSF - CF$$

3.1 Variations in pH Values of Precipitation

During the sampling period (May 2013 to July 2014), pH values of precipitation in the southern and northern slopes of Wushaoling Mountain showed similar variation ranges, with the average value slightly higher in the northern slope. Specifically, pH values ranged from 6.81 to 8.68 in the southern slope (average 7.50) and from 6.66 to 8.54 in the northern slope (average 7.55). Precipitation pH values were generally alkaline in both slopes. Seasonal variations are shown in Figure 1 [Figure 1: see original paper]. The average pH in precipitation was highest in summer for both slopes.

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

3.2 Variations in EC Values of Precipitation

In the southern slope, EC values ranged from 13.15 to 1086.00 s/cm (mean 156.07 s/cm), while in the northern slope they ranged from 17.28 to 971.50 s/cm (mean 179.60 s/cm) (Fig. 2 [Figure 2: see original paper]). In the southern slope, the highest EC value was observed on May 1, 2014, and the lowest on September 15, 2013. In the northern slope, the highest EC value occurred on April 24, 2014, and the lowest on August 11, 2013. At seasonal scales, EC values in the southern slope were lower than those in the northern slope. As shown in Figure 2c, EC values were higher in spring and winter than in summer and autumn, likely due to 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

Ion concentrations in precipitation in the northern and southern slopes are shown in Table 2 . Concentrations of Mg^{2}, Ca^{2}, NH , and SO^{2} differed significantly between slopes, while Na , K , Cl , NO , and F showed no significant differences.

In the southern slope, Ca^{2} and Na dominated cations (accounting for 83.58% of total cations), while SO^{2} dominated anions (accounting for 83.78% of total anions) (Fig. 3 [Figure 3: see original paper]). The chemical type was SO^{2}-Na , with these four ions accounting for 83.69% of total ion concentration. In the northern slope, Ca^{2} and Na also dominated cations (73.18% of total), SO^{2} dominated anions (83.82% of total), and the chemical type was SO^{2}-Ca^{2}-NO , with these four ions accounting for 79.77% of total ion concentration. The order of individual ion concentration percentages was similar between slopes: Ca^{2} > SO^{2} > Cl > Na > K > Mg^{2} > NH > NO > F > NO in the southern slope, and Ca^{2} > SO^{2} > Cl > Na > Mg^{2} > K > NH > NO > F > NO in the northern slope.

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

Ion	Southern slope (eq/L)	Northern slope (eq/L)
Ca^{2}	17.78±1.34A	12.26±1.06B
Mg^{2}	4.69±0.78a	1.95±0.31b
Na	15.69±1.83a	23.82±2.83b
K	1.70±0.18a	1.52±0.15a
NH	3.50±0.51a	2.74±0.34b

Ion	Southern slope (eq/L)	Northern slope (eq/L)
SO^{2}	10.40±0.90a	7.69±0.82b
NO	5.82±0.95a	4.69±0.78a
Cl	0.17±0.02a	0.15±0.06a
F	0.14±0.03a	0.11±0.01b
NO	0.11±0.01b	0.15±0.06a

Note: Mean±SE. Different uppercase letters within a column indicate significant difference between slopes at P<0.01 level; different lowercase letters indicate significant difference 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 scales, total ion concentration followed the order spring > winter > autumn > summer in the southern slope (Fig. 4a [Figure 4: see original paper]) and winter > spring > autumn > summer in the northern slope (Fig. 4b). In both slopes, Ca^{2} concentration was higher in spring than winter and higher in summer than autumn. SO^{2} concentration was highest in winter and spring in the northern and southern slopes, respectively. NO showed the same seasonal variation in both slopes: winter > spring > autumn > summer. Na showed identical seasonal variation in both slopes. Cl variation was winter > spring > autumn > summer in the northern slope and spring > winter > autumn > summer in the southern slope.

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

3.4 Relationships of Ions in Precipitation

Ion relationships are shown in Tables 3 and 4. SO^{2} showed significant correlations with Na , K , Mg^{2} , Ca^{2} , F , Cl , and NO in both slopes. In the southern slope, NO correlated significantly with Na , K , Mg^{2} , Ca^{2} , F , and Cl , while in the northern slope, NO correlated significantly with Na , K , F , and Cl . Cl correlated significantly with Na , K , Mg^{2} , Ca^{2} , and F in both slopes. NH showed significant correlations with SO^{2} and NO in the southern slope, indicating NH was the major neutralizing ion for SO^{2} and NO . Comparing correlation coefficients between slopes, those among Na , K , Mg^{2} , Ca^{2} , and NO were higher in the southern slope, while the coefficient between F and Cl was higher in the northern slope.

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

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

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

4.1 Sources of Ions in Precipitation

Ion concentrations were generally higher in the northern slope than in the southern slope, likely because the northern slope is nearer to sand dust sources, especially deserts. Additionally, many cement factories are distributed in the northern slope, increasing ion concentrations in precipitation. At seasonal scales, ion concentrations were relatively high in winter and spring in both slopes, possibly related to low precipitation, high wind speeds, and frequent sand dust events. Sand dust events increase terrigenous material in the atmosphere (Li et al., 2017b), inevitably increasing ion concentrations in precipitation. Conversely, ion concentrations were relatively low in summer and autumn, likely due to high precipitation amounts and dilution effects.

SO ^{2} originated mainly from local sources, including weathering of sulfate minerals (enrichment of CaSO and MgSO) and SO from industrial production and anthropogenic activities. Ca^{2} and Mg^{2} are important crustal components, reflecting significant influence from local source particles (Al-khashman, 2005; Eneroth et al., 2007; Li et al., 2014). NO originated mainly from anthropogenic activity emissions in the southern slope and from oil consumption and anthropogenic emissions in the northern slope. The average Na /Cl ratio was 0.73 in the southern slope and 0.81 in the northern slope (Table 2), lower than the seawater ratio (0.86) (Al-khashman, 2005; Eneroth et al., 2007), suggesting complex Cl sources from ocean, local sources, and anthropogenic activities. The K /Cl ratio was 0.36 in the southern slope and 0.34 in the northern slope (Table 2), higher than the seawater ratio (0.061), indicating negligible oceanic contribution to K and important roles for local sources and anthropogenic activities.

In the southern slope, the first three principal components explained 66.67% of total variance (Table 5). The first component explained 44.24% of variance with high loadings for all ions (except NH), suggesting local sources dominated. The second component explained 11.90% of variance with high NO loading, indicating contributions from industrial emissions, municipal waste incineration, and automobile exhaust. The third component explained 10.53% of variance with high NH and F loadings, reflecting contributions from industrial and agricultural production and organic decomposition.

In the northern slope, the first three components explained 64.83% of total variance (Table 5). The first component explained 40.78% of variance with high loadings for all ions (except NH), indicating local source dominance. The second component explained 13.07% of variance with high NH and F loadings, suggesting industrial and agricultural production and organic decomposition contributions. The third component explained 10.98% of variance with high NO loading, reflecting contributions from industrial waste gas emissions, municipal waste incineration, and automobile exhaust.

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

We used enrichment factor analysis to identify precipitation ion sources. Sources include anthropogenic activities, terrigenous material, and sea salt aerosol (Al-khashman, 2005; Li et al., 2014, 2015, 2016; Guo et al., 2015). We calculated [Cl /Na]precipitation = 1.35[Cl /Na]ocean and [Mg^2 /Na]precipitation = 0.47[Cl /Na]ocean for the southern slope, and [Cl /Na]precipitation = 1.24[Cl /Na]ocean and [Mg^2 /Na]precipitation = 0.58[Cl /Na]ocean for the northern slope, suggesting Na was the oceanic reference ion (Xiao et al., 1993).

Enrichment factors are shown in Table 6 . EFcrust values for Na were generally <1 in both slopes, indicating crustal derivation. EFcrust values for K were much <1 while EFocean values were much >1, suggesting crustal dominance. For Mg^2 , EFcrust values were <1 while EFocean values were >1 in both slopes, indicating crustal origin. EFcrust values for Cl ranged from 46.83 to 138.05 in the southern slope and 108.93 to 326.84 in the northern slope; only in autumn in the northern slope was EFocean >1, suggesting oceanic dominance. EFcrust values for NO were >717.07 in both slopes, indicating negligible oceanic and crustal contributions and dominant anthropogenic sources. EFocean values for SO ^{2} were also >717.07, indicating anthropogenic dominance. EFocean values for Ca^2 ranged from 89.66 to 212.01 in the southern slope and 35.61 to 102.11 in the northern slope, suggesting crustal origin. EFocean values for F were >1 in both slopes, indicating crustal sources.

We calculated source contributions of sea salt fraction (SSF), crust fraction (CF), and anthropogenic fraction (AF) to further determine ion sources (Equations 3-5) (Mahlknecht et al., 2004; Li et al., 2015). Results are shown in Table 7 . NO originated mainly from anthropogenic activities (99.64% in southern slope, 99.69% in northern slope). Only a small portion of SO ^{2} came from oceanic and crustal fractions. Crustal and anthropogenic contributions for Mg^2 and K were 76.00% and 93.75% in the southern slope, and 80.35% and 93.43% in the northern slope, respectively. F was mainly affected by crust and anthropogenic activities (87.86% and 76.18% in southern and northern slopes, respectively). Unlike other ions, Cl originated mainly from sea salt fraction (98.83% and 99.53% in southern and northern slopes, respectively).

Table 6 Enrichment factors of ions in precipitation in the southern and northern slopes of Wushaoling Mountain

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

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

4.2 Indicative Significance for Sand Dust Events

To study precipitation chemistry indications of sand dust events, we selected three typical events based on event frequency and precipitation timing: May 22, 2013; April 23-24, 2014; and April 30, 2014. For all three events, precipitation occurred after the sand dust events.

As shown in Figure 5 [Figure 5: see original paper], Na exhibited high concentrations after sand dust events in both slopes. As previously analyzed, Na originated mainly from terrigenous material, and sand dust events increased atmospheric terrigenous material, raising Na concentrations in precipitation. After sand dust events, K , Mg^{2} , SO ^{2} , NO , and Ca^{2} concentrations increased in the southern slope but decreased in the northern slope. Two possible reasons exist: these ions originated mainly from terrigenous material and anthropogenic activities, and large quantities of sand dust were transported to the southern slope during events, increasing ion concentrations there while decreasing them in the northern slope. Cl concentration increased after sand dust events in both slopes, indicating sands and dusts contained high NaCl concentrations.

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

5 Conclusions

During the sampling period (May 2013 to July 2014), precipitation pH values in the southern and northern slopes of Wushaoling Mountain showed similar variation ranges, with the northern slope average slightly higher. EC values were higher in the northern slope than in the southern slope. Concentrations of Mg^{2} , Ca^{2} , NH , and SO ^{2} differed significantly between slopes. The chemical type of precipitation was similar in both slopes: SO ^{2} -Na . Land sources (including terrigenous material and anthropogenic activities) played important roles in determining ion concentrations in both slopes (except Cl). Cl originated mainly from sea salt fraction. After sand dust events, Na concentration increased in both slopes. Furthermore, K , Mg^{2} , SO ^{2} , NO , and Ca^{2} concentrations increased in the southern slope but decreased in the northern slope. These results help further understand atmospheric pollution caused by sand dust events in Wushaoling Mountain and provide a scientific basis for effective prevention of atmospheric pollution in this region.

Acknowledgments

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Note: Figure translations are in progress. See original paper for figures.

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