ORIGINAL ARTICLE

Composition of wet deposition in the central Qilian Mountains, China

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Abstract A total of 90 individual precipitation samples have been collected in the central Qilian Mountains from August 2012 to November 2013. All samples were analyzed for major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}), anions (Cl^-, NO_3^- and SO_4^{2-}) and conductivity. Precipitation EC ranged from 2.26 to 482 μc/cm with an average value of 41.9 μs/cm. Precipitation was of SO_4^{2-}-Mg^{2+}-Ca^{2+} type, and these three ions contributed >70 % to the total ionic concentration. Precipitation events occurred around summer displayed lower concentrations, whiles it had higher concentrations in winter and spring with little precipitation and larger wind speed. The major sources for these ions are regional crustal aerosols and species from central Asia and northwestern China arid regions brought by the westerly, and some aerosols from human pollution are secondary sources. It is also interesting that precipitation chemistry is different under diversely atmospheric circulation in Hulugou basin: the monsoon precipitation, the interaction precipitation influenced both by monsoon and westerly, and the westerly precipitation events.

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Introduction

Atmospheric precipitation is an important means of scavenging pollutants from the atmosphere and this occurs either by wet or by dry deposition (Migliavacca et al. 2005), and so the chemical composition of precipitation or snow/firn is strongly affected by the chemical composition of the atmosphere (Al-Khashman 2005; Kang et al. 2002, 2003, 2004, 2007a, b). Studies on precipitation chemistry are important in evaluating air quality and understanding anthropogenic contributions to atmospheric chemistry/environment. The change in chemical composition of precipitation can indirectly reflect the atmospheric quality of specific region, which is a particularly sensitive indicator of pollution emissions (Calvo et al. 2010). Knowledge of the chemical composition of precipitation can also provide information of the regional and long-range transport of anthropogenic aerosols and its impact on ecosystems through deposition processes (Mphepya et al. 2004; Li et al. 2007). Precipitation composition can be influenced by many factors, such as local emissions, regional-scale pollutants transport processes, meteorological conditions, and sea level elevation (Sickles and Grimn 2003; Calvo et al. 2010; Rocha et al. 2003; Tang et al. 2005; Zhao et al. 2008) and geographical characteristics; elevation difference may influence the chemical composition of rainwater at a particular point in time and in a particular location. Therefore, chemical composition of rainwater varies from site to site and region to region. Moreover, different climate conditions also influence trace substance concentrations in the rainwater (Baron and Denning 1993). Numerous studies

have been conducted on precipitation chemistry from different regions of the world (Zhang et al. 2003a, b; Ali et al. 2004; Basak and Alagha 2004; Mphepya et al. 2004; Lehmann et al. 2005; Tu et al. 2005; Zimmermann et al. 2006; Li et al. 2007, 2008, 2009a, b; Huang et al. 2008; Celle-Jeantonet al. 2009; Calvo et al. 2010; Dong et al. 2011).

Precipitation chemistry in background sites is of great interest and useful in the study of air pollution. The atmospheric composition of rainwater measured at sampling sites far from the direct impact of anthropogenic sources is useful as a reference level for the geographic area and, in addition, it can be to determine the extent of anthropogenic contamination even in these remote areas (Calvo et al. 2010). In recent decades, great efforts have been devoted to exploring the climatologic and hydrological signals of precipitation in Qilian Mountains and adjacent regions by way of stable isotope studies (Zhang and Wu 2007a, b, 2009; Wu et al. 2010; Zhao et al. 2011; Ma et al. 2012). However, few studies have focused on chemical composition of rainwater either in rural or in urban areas in Qilian Mountains. Thus, research on rainwater chemistry in this area is necessary to detect and evaluate air quality and the relative contribution of different sources of atmospheric pollutants. Based on the samples collected at the Qilian Alpine Ecology and Hydrology Research Station (Hulugou Station, 30°47′N, 90°58′E, 3260 m.a.s.l) (Fig. 1) during August 2012 to November 2013, central Qilian Mountains, here the chemical composition of individual precipitation events are reported. The purpose of this study is as follows: (1) to characterize the chemical composition in precipitation during wet season, and to identify the possible sources of the various constituents; (2) to investigate the seasonal variability of precipitation chemistry in this unique region, and to confirm whether the central Qilian Mountains as a representative background site for atmospheric precipitation. In addition, this study also made comparison with other researches in neighboring regions.

The study area, precipitation sampling and data analysis

Study area

Qilian Mountains (92–107°E, 36–43°N) lies in the northeastern edge of Tibetan Plateau of China. It is made up of several parallel mountains and valleys, stretching 850 km long from northwest to southeast and extending 200–300 km wide from south to north. The altitudes about 30 % of mountains are above 4,000 m in Qilian Mountains, and its highest peak is Tuanjie Peak with altitude of 5,826.8 m. There are 2,859 glaciers in Qilian Mountains, with an area of 1,972.5 km^2, and the total reserves of glacier are 954.38×10^8 m^3 (Wang et al. 2011). The temperature varies by the altitude fluctuation from valley to mountain. The annual precipitation, appearing a decreasing trend from east to west and from south to north, varies from 400 to 700 mm. The Qilian Mountains is very important to
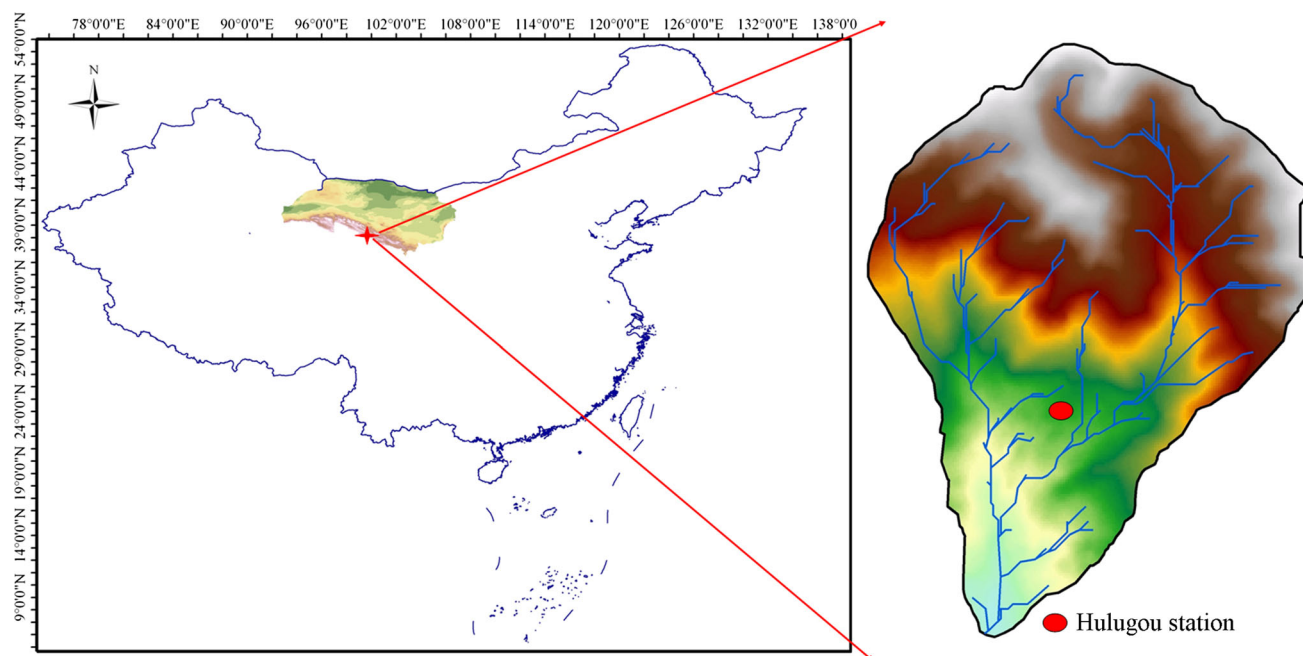

Fig. 1 The location of Hulugou basin

Hexi oasis because it is the sources of Shiyanghe, Heihe, Shulehe River coming from precipitation and melting water. The Hulugou basin is in the central Qilian Mountains, Qinghai Province, China, at $38°12'14''$–$38°16'23''$N and $99°5'37''$–$99°53'54''$E (Fig. 1) and has a catchment area of 23.1 km². It is the representative of Qilian Mountains, and is well suited for cold alpine catchment research. The altitude ranges from 2,960 to 4,820 m. The basin is very cold and has little evaporation (Yang et al. 2013). The basin is the water source of Heihe River. The terrain is complex and there is a clear vertical zonation of the vegetation: landscape zones include glacier/snow, alpine cold desert, marsh meadow, alpine shrub, and mountain grassland.

Precipitation sample collection and laboratory analysis

Precipitation samples were collected for each precipitation event at Hulugou basin in the altitude of 3,260 m. Samples collector was placed on the rooftop (8 m above the ground and 1 m from the floor of the roof) away from the surface soil and any specific pollutant sources. Sampling was done manually on event basis using wet collector, which was fitted with a 5-L polyethylene collecting flask (at the bottom) and polyethylene funnel 26 cm in diameter. The collected rainwater or snow was then loaded into the pre-cleaned polyethylene sample bottles after each precipitation event. The collectors (flasks and funnels) were deployed at the onset of each precipitation event and were retrieved immediately after the flasks were filled up or after the rainfall stopped. Prior to installation of collectors, the funnels and flasks were carefully cleaned and dried before use. In addition, stringent sampling protocols were followed at all times during sample collection and handling to assure samples was not contaminated at the 0.1 μeq/L level (Al-Khashman 2005). Precautions were taken in both collection and analysis processes to avoid the possible contamination of rainwater samples. A total of ninety event-based precipitation samples were collected at Hulugou station from August 2012 to November 2013 (Fig. 1). After collection, all samples were immediately sealed in plastic bags and stored in a cold laboratory at −18 °C. Before analysis, they were stored at 4 °C in a refrigerator, so that they could melt gradually without evaporation. During sample collection, precipitation amount, air temperature, wind speed and humidity were recorded at the Hulugou automatic meteorological station. Cations were analyzed with a Dionex-600 Ion Chromatograph and anions with a Dionex-2500 Ion Chromatograph in Gansu Hydrology and Water Resources Engineering Research Center, Cold and Arid Region Environment and Engineering Research Institute, Chinese Academy of Sciences. The analytical precision reached 10^{-9} g/mL and the standard deviation is less than 5 %.

Evaluation of ion source from weathering

According to Gibbs' diagram (Gibbs 1970), solutes in terrestrial water are from two primary sources of rainfall and rock weathering. To evaluate the importance of rock weathering source for ions in precipitation, a reputed enrichment factor (EF), using Ca^{2+} as the reference element for soil sources and Na^+ as the reference element for marine sources, was calculated (Vermette et al. 1988; Okay et al. 2002; Ma et al. 2012) such that:

$$EF_{soil} = [X/Ca^{2+}]_{watersample}/[X/Ca^{2+}]_{soil} \qquad (1)$$

$$EF_{marine} = [X/Na^+]_{precipitation}/[X/Na^+]_{marine} \qquad (2)$$

where X is concentration of interested ion, and water sample can be precipitation, river water, or groundwater. In this study, the ratio $[X/Ca^{2+}]_{soil}$ of respective interested ion is derived from Okay et al. (2002), and the $[X/Na^+]_{marine}$ ratio of respective interested ion is based on the seawater composition (Keene et al. 1986). Generally, EF ≤ 1 indicates that the interested ion in water is diluted by sea salt, and EF ≥ 1, enrichment of interested ion by soil (Zhang et al. 2007). All concentrations' units used in Eqs. (1) and (2) are mol/L.

Furthermore, the contribution of non-sea salt part of ionic concentration (P) in precipitation can be calculated with Eq. (3) (Li et al. 2009a) such that:

$$P = [A - (R \times M)]/A \qquad (3)$$

where A is the ionic concentration, M is the concentration of tracer ion, and R is the ratio of X (other ions)/Na^+ in standard seawater, such as $Cl^-/Na^+ = 1.165$ and $Mg^{2+}/Na^+ = 0.227$. Na^+ was determined as the sea salt tracer ion in this study.

Trajectory analysis and water vapor flux

Although trajectories indicate the general, rather than the exact, flow of air parcels, they have proved of considerable value in many studies of the transport of atmospheric components (Asaf et al. 2005; Eneroth et al. 2007; Barras and Simmonds 2008; Li et al. 2009a, b; Theakstone 2011). The HYSPLIT4 model (http://www.arl.noaa.gov/ready/hysplit4.html), a complete system for computing trajectories, can be used to carry out complex dispersion and deposition simulations. The 10-days backward trajectories with a daily resolution have been used to investigate the pathways of the air masses arriving at the sampling site (38.25°N, 99.88°E, 5,500 m.a.s.l.) at 12:00 Beijing time (04:00 UTC). Monthly mean geopotential height, wind fields, relative humidity and air temperature at 700 hPa were obtained from the National Oceanic and Atmospheric Administration-Cooperative Institute for Research in

Environmental Sciences (NOAA-CIRES) Climate Diagnostics Center reanalysis R1 dataset (available from http://www.cdc.noaa.gov/) (Kalnay 1996; Kistler et al. 2001). To quantify changes in large-scale atmospheric circulation, mean circulation composites from spring to winter during 2012–2013 were obtained. The details about the calculation for water vapor flux were shown in the previous studies (Li et al. 2011, 2012).

Results

EC and chemical composition

The average value for total anions, 137.2 µeq/L and the average value for total cations, 281.5 µeq/L showed larger gap each other in Hulugou basin. In Fig. 2a, the slope, 2.0, suggesting at least one major anion is missed. Since the soil around the sources region of Heihe River is calcareous and alkaline, the observed anion deficiency is more likely due to the exclusion of HCO_3^- from the measurements. Also,
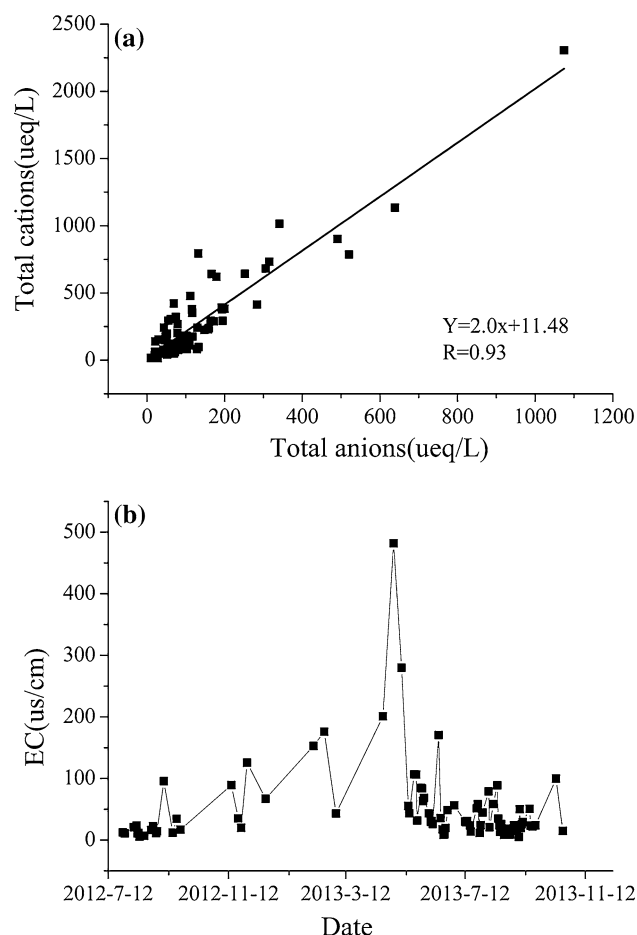

the regression ($R = 0.84$) showed a relative high correlation between total anions and total cations, suggesting that the main cations, Na^+, Mg^{2+}, Ca^{2+}, K^+ and main anions Cl^-, NO_3^-, SO_4^{2-}, were a general balance. The conductivity ranged from 5.26 to 482 µs/cm with a mean value of 41.9 µs/cm. EC was correlated with all ions but not including NO_3^-, and mainly showed positive correlation with SO_4^{2-}, Ca^{2+} and Mg^{2+} ($r = 0.82$, 0.88 and 0.9, respectively). This indicated that the EC was controlled by alkaline earth elements and could explain why precipitation in this region was not acidic. As shown in Fig. 2b, it is intuitively clear that high precipitation alkalinity was generally associated with winter and spring days, when sandstorm activities were also frequent, whereas low-quantity sandstorms in turn lead to low EC values during the wet season (May–October). The mean EC values for spring, summer, autumn and winter are 105, 29, 43 and 130 µs/cm, respectively. As a consequence of this variability, the highest alkalinity was observed on 30 April 2013 with an EC of 482 µs/cm, and the lowest alkalinity on 5 September of 2013 with an EC of 5.26 µs/cm.

The average ionic concentrations for Cl^-, SO_4^{2-}, NO_3^-, Na^+, K^+, Mg^{2+} and Ca^{2+} were 42, 67.3, 27.9, 32.1, 13.3, 44.4 and 191.7 µeq/L. Among them, Cl^- and SO_4^{2-} dominated anions and accounted for 79.6 % of total anions composition, while Mg^{2+} and Ca^{2+} dominated cations with a contribution of 83.8 % (Fig. 3). Precipitation was of SO_4^{2-}-Mg^{2+}-Ca^{2+} type, and these three ions contributed >70 % to the total ionic concentration. SO_4^{2-}, Mg^{2+} and Ca^{2+} accounted for 16, 11 and 46 % of the total ionic concentration, respectively. The order of cations' concentrations for precipitation ($Ca^{2+} > Na^+ > K^+ > Mg^{2+}$) in Hulugou basin was the same as that of standard crustal materials ($Ca^{2+} > Mg^{2+} > Na^+ > K^+$), while the order of anions' concentrations in precipitation ($SO_4^{2-} > Cl^- > NO_3^-$) differed from that of standard seawater ($Cl^- > SO_4^{2-} > NO_3^-$), which indicated the control exerted by crustal materials on the chemical composition of precipitation in study region. High Cl^- and Na^+ concentration was due to the rainfall scavenging of desert dust aerosols (nearby the Badain Jaran Desert and Kumtag Desert). However, Ca^{2+} and SO_4^{2-} concentrations vary

Fig. 2 Linear regression of total cations and anions (**a**) and the temporal variation of EC in precipitation samples (**b**)
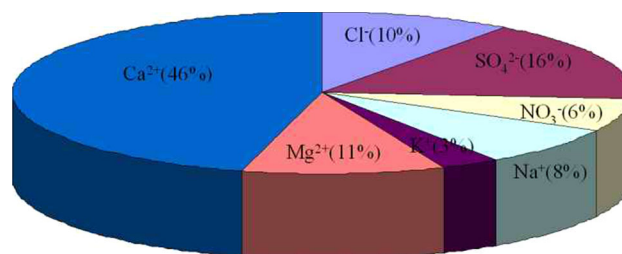

Fig. 3 Percentage of ions to total ion mass in precipitation

widely with various individual precipitation events. Concentrations of the two ions (Fig. 4, taking Ca^{2+} as an example) were the highest following dry periods or during the periods with little precipitation, but it also showed the lowest values during the continuous precipitation events. This suggested that precipitation amount may affect their concentrations since heavy precipitation can wash crustal aerosols out of the air. The large contribution of Ca^{2+} is mainly due to the influence of continental dust rich in calcium (Li et al. 2007; Zhang et al. 2003b).

Seasonal variations of precipitation chemistry

As shown in Fig. 5, the cations and anions' concentrations showed great seasonal variation in the central Qilian Mountains. Precipitation events occurred around summer displayed lower concentrations, while it had higher concentrations in winter and spring with little precipitation and larger wind speed (Table 1; Fig. 5). All ions exhibited absolutely higher concentrations in precipitation events after October. During the dry season (the dry season is the period from October to April of the following year), precipitation was characterized by higher ion concentrations and a gradual build-up of pollutants relative to wet season. Furthermore, higher amounts of particulate matters in suspension in the air are usually expected during dry season, resulting in higher concentrations of these ions in precipitation (Fan et al. 1999; Hontoria et al. 2003; Migliavacca et al. 2005). However, sporadic high ion concentrations during wet season indicated frequent precipitation events with occasional dust campaigns and anthropogenic activities. This reveals that the soil-derived crust particulates in atmosphere were deposited with the less rainfall events occurring around winter and spring under the frequent sandstorms. Strongly elevated ion concentrations during sandstorm rainfall were also observed in adjacent areas, such as the Tengger Desert and the central
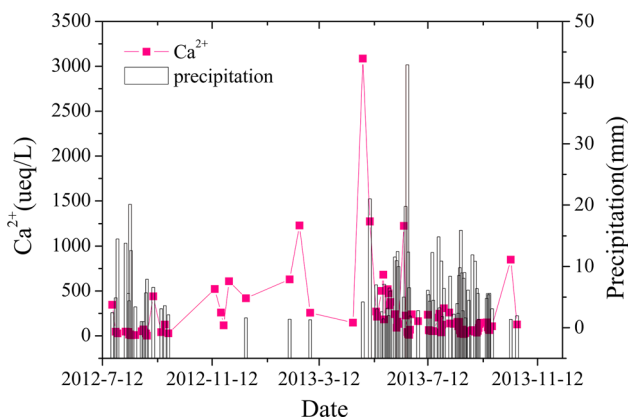

Fig. 4 Comparison between Ca^{2+} concentrations and precipitation amount

reaches of Heihe River (Feng et al. 2004). It is also obvious that the month occurred in the maximum and minimum is different among ions. Cl^- and SO_4^{2-} showed two peaks in February and April of 2013, and the minimum is occurred in June and July. NO_3^- had the highest concentrations in April 2013 and two higher values in November 2012 and October 2013. The maximum for Na^+, K^+ and Ca^{2+} also happened in April 2013, while Mg^{2+} occurred in February and April of 2013.

Based on the metrological observation, the precipitation in dry season (the period from October to April of the following year) only accounted for 3.1 % of total precipitation during the sampling period, whereas the concentration for Cl^-, SO_4^{2-}, NO_3^-, Na^+, K^+, Mg^{2+} and Ca^{2+} is 4.2, 5.93, 2.94, 1.47, 2.93, 2.11 and 3.79 times higher in dry season than that in wet season, respectively, which is also higher than that of average values during sampling period. The ionic concentration in precipitation varied seasonally due to the influence of precipitation amount, and the largest composition generally occurred at less precipitation amount (Table 2). The ionic concentrations decreased exponentially with increasing precipitation (Fig. 6, taking Cl^- as an example). This suggested that precipitation may affect their concentration through a dilution effect, which can also be reflected by the decreased ionic concentration during the constituent precipitation events. For example, the total cations and anions decreased from 97.41 to 132.81 µeq/L in 10 August 2012 to 10.0 µeq/L and 117.08 µeq/L in 13 August 2012, and the similar phenomenon also occurred in precipitation events during 29–31 May 2013, 7–9 June 2013, 14–27 July 2013 and 16–19 September 2013. This also confirmed that the heavy precipitation can wash crustal aerosols out of the air.

Correlations among different components

Three factors (principal components, PCs) with eigenvalues >0.6 explained 92 % for the precipitation chemistry (Table 3). The PC1 value (65 %) had high loadings of all ions but not including NO_3^-; these are mainly related to soil sources. The significantly positive correlations among these ions and their high concentration may result from a large contribution by terrigenous sources, which contain large amounts of $CaSO_4$ and $MgSO_4$. Ca^{2+} and Mg^{2+} probably originated from natural sources (soil and dusts) and they contribute to the neutralization reactions that occurred in the atmospheric precipitation. The Ca^{2+} and Mg^{2+} are also frequently found in the areas rich in limestone, which might explain the association of both species in the same factor. The PC2 value accounts for 23 % of the variance; it is loaded for NO_3^-, which is mainly associated with anthropogenic sources and local biogenic sources came from regional activities such as dung combustion for
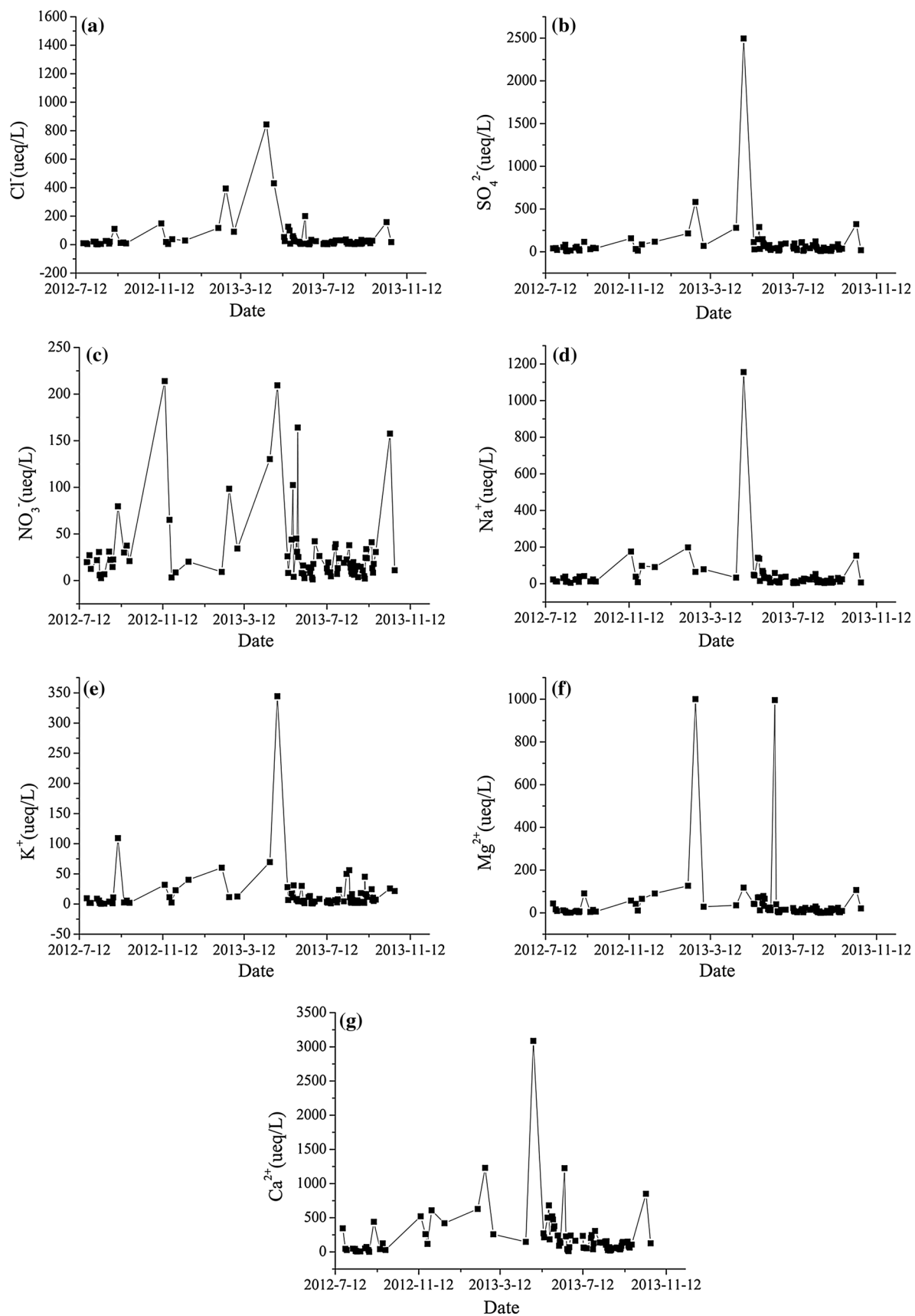
Fig. 5 Seasonal variation of cation and anion concentration in atmospheric precipitation samples in the central Qilian Mountains

heating and cooking and the excretion of yaks and horses. PC3 value accounts for 7 % of the variance; it is loaded for Na^+, which may reflect the influence of marine or desert sources.

The significantly positive correlation of Cl^- with K^+ and Na^+ suggested a common origin (Table 4), and three ions were probably influenced by both local soil and the marine source. In addition, the positive correlations among Cl^-, Mg^{2+} and Ca^{2+} also reflected the influence of terrestrial weathering on Cl^-: on the one hand, Na^+ and Cl^- may also be dominated by local soil sources with the highest values; on the other hand, some Na^+ and Cl^- may originate from soil dust aerosols that contain a large component of halite (NaCl, an important component of sand in the surrounding desert areas). The average Na^+/Cl^- ratio was 0.21, much lower than that in seawater (0.86), suggesting that precipitation was enriched in Cl^-. Thus, the data may indicate that the Cl^- in precipitation at the central Qilian Mountains had complex sources (including marine, soil dusts and anthropological sources). The K^+/Cl^- ratio (0.32) is much higher than that of sea water (0.061), suggesting that K^+ may not originate from the ocean. Generally, there are three main sources for the dissolved solids in precipitation: sea salt aerosols, terrestrial aerosols (soil dust, biological emissions) and anthropogenic sources (such as industrial and agricultural activities, burning of vegetation and fossil fuel). However, human activities around the research site are minimal. So K^+ mainly came from local or regional mineral aerosols. Some studies have also suggested that desert dusts on Hexi corridor are an important source of precipitation by means of convective precipitation (Ma et al. 2012).

The positive correlation between SO_4^{2-} and NO_3^- can be found (Table 4), which indicated the contribution from human pollution on the concentration of SO_4^{2-}. High positive correlation has also been found between SO_4^{2-} and Ca^{2+} because local soil is rich in sulfates such as gypsum and mainly contains Ca^{2+}, Mg^{2+} and SO_4^{2-} (Table 4). This suggested that Ca^{2+} and SO_4^{2-} are the result of the dissolution of gypsum aerosol, so that the ionic composition of precipitation was chiefly derived from the dissolution of gypsum aerosols, and the dissolution of dolomite aerosols was the second dominant. So sulfate minerals dominated the precipitation chemistry in the central Qilian Mountains. In addition, there is no correlation between Mg^{2+} and SO_4^{2-} (Table 4), which reflected that the Mg^{2+} is not dominated by $MgSO_4$, while mainly contributed by carbonate aerosols. The NO_3^- only displayed the positive correlation with K^+ and Ca^{2+} (Table 4), and this also reflected that it mainly sourced from atmospheric pollutants. The significantly positive correlation of Na^+ with Mg^{2+} and K^+ indicated a contribution of crustal materials to magnesium and potassium (Table 4). The contribution by crustal sources on the concentration of K^+ with Mg^{2+} and Ca^{2+} can be also indicated by the statistically positive correlation (Table 4). A significant correlation was also found between Mg^{2+} and Ca^{2+}, similar to the temporal trend found during the sampling period (Fig. 5), suggesting a common crustal source species.

Table 1 Seasonal values of major ion (μeq/L) concentrations and conductivity (μs/cm) in the central Qilian Mountains

	Temperature (°C)	Relative humidity (%)	Precipitation (mm)	Wind speed (m/s)	EC	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
Spring	−1.83	62.86	21.98	2.12	105.23	328.87	153.58	71.50	59.14	31.73	38.44	266.80
Summer	9.14	77.35	102.09	1.64	29.17	19.98	47.09	18.17	22.59	8.77	34.16	132.30
Autumn	−1.57	73.17	17.71	1.74	42.89	50.49	83.81	59.91	48.39	20.61	34.89	259.52
Winter	−11.49	56.61	2.55	2.76	130.40	144.50	249.84	34.16	112.84	33.73	320.79	721.84

Table 2 The mean values of ionic concentrations (μeq/L) in different precipitation ranks

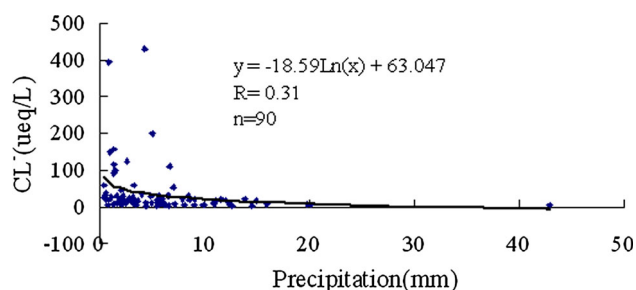| Precipitation ranks (mm)	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
>20	6.34	29.40	8.85	11.02	8.22	13.29	77.79
10–20	11.74	39.22	12.34	16.99	7.35	9.22	83.38
5–10	20.17	43.02	21.89	20.22	13.03	16.47	130.54
2–5	48.99	166.43	31.81	79.48	25.56	65.20	324.12
1–2	50.47	102.82	37.43	63.26	16.71	44.08	298.25
<1	82.72	130.15	59.02	52.84	18.88	139.28	390.56

Fig. 6 The chloride concentration in precipitation, showing the influence of the amount of precipitation

Table 3 Factors loading for major ion concentrations in precipitation at the central Qilian Mountains

	Component				
	1	2	3	4	5
Cl^-	0.880	−0.277	0.252	−0.072	−0.279
SO_4^{2-}	0.739	0.580	−0.297	−0.060	−0.082
NO_3^-	0.448	0.703	0.011	−0.024	0.104
Na^+	0.821	−0.511	0.541	−0.142	0.172
K^+	0.936	−0.024	−0.166	−0.267	0.070
Mg^{2+}	0.778	−0.523	0.094	0.320	0.043
Ca^{2+}	0.828	0.422	−0.207	0.286	0.023
% of variance	62 %	23 %	7 %	4 %	2 %

Table 4 The correlation coefficients for the species in precipitation collected from the central Qilian Mountains

Correlation	Cl^-	SO_4^{2-}	NO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1.000						
SO_4^{2-}	**0.44**	1.000					
NO_3^-	**0.31**	**0.57**	1.000				
Na^+	**0.83**	**0.31**	0.04	1.000			
K^+	**0.79**	**0.72**	**0.33**	**0.81**	1.000		
Mg^{2+}	**0.82**	0.23	0.03	**0.86**	**0.65**	1.000	
Ca^{2+}	**0.54**	**0.89**	**0.55**	**0.43**	**0.73**	**0.49**	1.000

Boldfaced values are statistically significant ($n = 90$, $P < 0.05$)

Discussion

Enrichment factors

Possible sources of constituent ions in precipitation have been identified by enrichment factors (EF) (Vermette et al. 1988; Okay et al. 2002). Most of the chlorine in Hulugou Basin was influenced both by the sea and soil. Cl^- EF(sea) values were much lower than one but the EF(soil) values were much higher than ten (Table 5). EF(sea) values of Ca^{2+} ranged between 18 and 293, suggesting that most of

Table 5 The EF enrichment factor values in precipitation collected from the central Qilian Mountains

Relative to the sea (EF)sea	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
Spring		418.76		73.63	94.35	768.55
Summer		39.62		6.89	24.42	112.95
Autumn		71.66		18.87	30.83	257.68
Winter		221.52		29.66	311.31	717.55

Relative to the soil (EF)soil	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
Spring	125.12		1.03	0.23	0.52	
Summer	62.30		0.51	0.14	2.33	
Autumn	63.12		0.33	0.16	1.29	
Winter	64.58		0.27	0.09	5.08	

the calcium came from the soil, whereas Mg^{2+} appears to be dominated by soil indicated by the fact that EF(sea) values and the EF(soil) values were much higher than one (Table 5). K^+ appears to be mainly influenced both by the sea and soil owing to the lowest EF(soil) values but the higher EF(sea) values. These EF values also confirmed the weak anthropogenic contributions in Hulugou basin. EF(sea) values of SO_4^{2-} were between 44 and 336, implying that the sea was not the main source for it. Na^+ exhibited a clearly marine origin with EF(soil) values between 0.1 and 0.9 with a mean value of 0.55. For seasonal variation, Cl^- EF(sea) and Ca^{2+} EF(sea) showed the increasing trend from spring to winter with the maximum in February and June of 2013, respectively, while K^+ EF(sea) is higher in summer and autumn. For Mg^{2+} EF(sea), the maximum and minimum occurred in winter and spring, respectively (Table 5). For EF(soil) values, the Cl^-, Na^+ and K^+ showed decreasing trend from spring to winter, and vice versa for Ca^{2+}. These variations may be influenced by precipitation amount. It is interesting that the Cl^- EF(value) and Na^+ EF(value) values have no correlation with metrological elements at sampling site, whereas the positive correlation for K^+ EF(value) with the relative humidity ($R = 0.45$) and the vapor pressure ($R = 0.41$) confirmed the influence from local weather conditions. However, the Ca^{2+}EF(sea) had the negative correlation with wind speed, which also reflected the great contribution from local terrigenous sources ($R = -0.35$). In addition, the influence from continental crusts can be also confirmed by the correlation: between K^+ EF(sea) and wind speed ($R = -0.3$), between K^+ EF(soil) and temperature.

Non-sea salt contribution

Using Eq. (3), the calculated non-sea salt source percentages for SO_4^{2-}, K^+, Mg^{2+} and Ca^{2+} were 99.8, 97.4, 96.6

and 98.9 %, respectively, and non-sea sources played an important role in determining the ionic composition. There are four explanations for this. (1) Marine moisture contributed little to ions inputs, while dusts imported from the central Asia and Northwestern China regions by the westerly making great contribution to ion concentrations, which can be also supported by the higher composition in winter and spring. (2) The study area is located at the northeastern margin of Tibetan plateau and the plateau monsoon has some influence on regional climate in spring and winter. (3) The sampling site is nearby the Badain Jaran Desert and Tenger desert, so that these desert dusts can be also imported by local circulation. (4) There is some dust from human pollution because Hexi corridor is an important industrial base of Gansu Province, especially for SO_4^{2-} and NO_3^-. Owing to the longest linear distance from study region to the nearest coast exceeding 1,000 km, consequently, when the vapor is transported, continuous exchanges and reactions between terrestrial material and the atmosphere alter the chemical composition, such that the precipitation composition was different from that in sea water. For example, the reaction between sea salt particles and H_2SO_4 can cause the enrichment of Cl^- in precipitation and depletion in aerosol (Hitchcock 1980; Shrestha et al. 1997). This can be also explained the Cl^- enrichment in Hulugou basin.

Due to the very low concentration for NO_3^- in sea water, the NO_3^- detected in precipitation is considered to have been only from soil and anthropogenic sources. According to Safai et al. (2004) and Huang et al. (2008), SO_4^{2-} is also derived from sea water, soil and anthropogenic sources. The ratios of NO_3^-, SO_4^{2-} and Cl^- to Na^+ were used as the index to make a distinction between rock weathering and human activities as the sources of the precipitation ions in this study (Fig. 7). It was also shown that positive correlations have existed between Na^+ normalized NO_3^- and SO_4^{2-} values in precipitation, suggesting their same source. The precipitation had NO_3^-/Na^+ (1.08) and SO_4^{2-}/Na^+ (2.67) ratios higher than 1, indicating the influence from anthropogenic input on these two ions (Fig. 7). The contribution of NO_3^- and SO_4^{2-} from soil can be calculated using the ratio of NO_3^- or SO_4^{2-} to Ca^{2+}. In our study, about 61.9 % of the NO_3^- was contributed by anthropogenic sources. Approximately, 38.1 % of the SO_4^{2-} was originated from anthropogenic sources, while 62.7 % was from soil sources and only 0.2 % from marine sources. For seasonal contribution, the anthropogenic input has accounted for 83.2, 30.5, 71.9 and 96.1 % in spring, summer, autumn and winter for NO_3^-, and the value for SO_4^{2-} is 56.1, 4.7, 57.2 and 69.1 %, respectively. The results indicated that: (1) the contribution from soil source on SO_4^{2-} was higher than that of anthropogenic sources, in contrast to previous reports (Zhang et al. 2007;
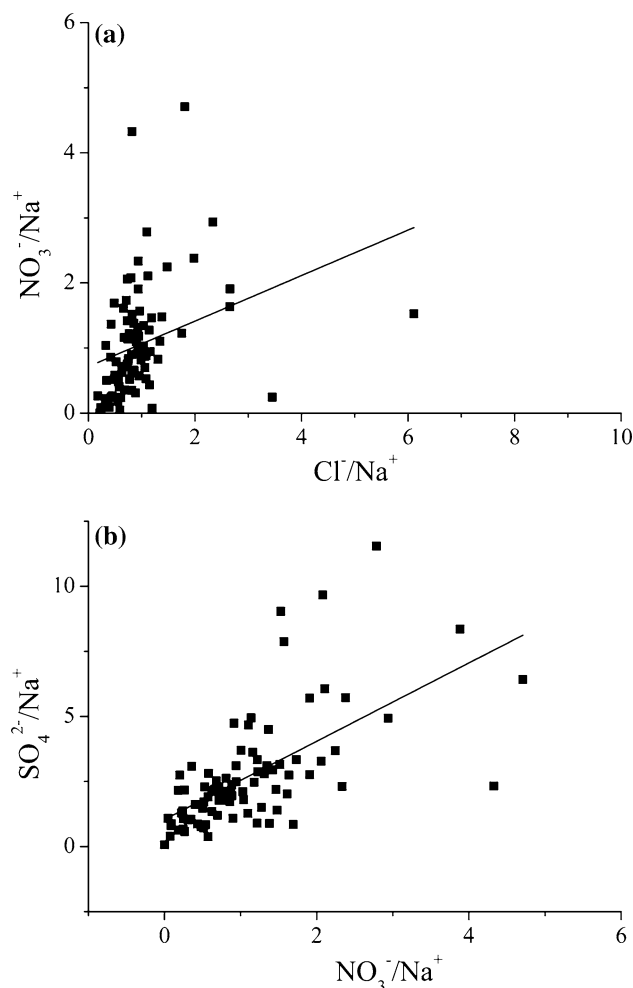

Fig. 7 Plots of NO_3^-/Na^+ versus SO_4^{2-}/Na^+, Cl^-/Na^+ versus NO_3^-/Na^+ molar ratios in wet season

Huang et al. 2008); (2) SO_2 from anthropogenic input could have formed SO_4^{2-} which reacted with crustal components like Ca^{2+} and Mg^{2+} to form sulfates, explaining the significant correlation between SO_4^{2-} with Ca^{2+}; (3) the contribution from anthropogenic source on NO_3^- is much larger than the soil source; and (4) the great influence from anthropogenic input mainly occurred in winter and spring.

Back trajectories and water vapor transportation

Back trajectories indicated that the westerly mainly crossed the arid regions of central Asia and then to the central Qilian Mountains (Fig. 8). In addition, some trajectories also were from the Indian Ocean or the Pacific Ocean by monsoon circulation, across industrial areas during wet season. Air masses bringing dusts to study region in dry season generally traveled from one of the three directions: from the dust sources region in Asia: Central/West Asia, from Northwestern China or from the Hexi corridor

(Fig. 8). The monthly water vapor also confirmed precipitation mainly sourced from the westerly in winter, spring and autumn at 700 hPa, so it also confirmed that the dusts

from arid regions mainly dominated the precipitation chemistry in Hulugou basin (Fig. 9). However, the monsoon also can arrive at the study region in summer, which
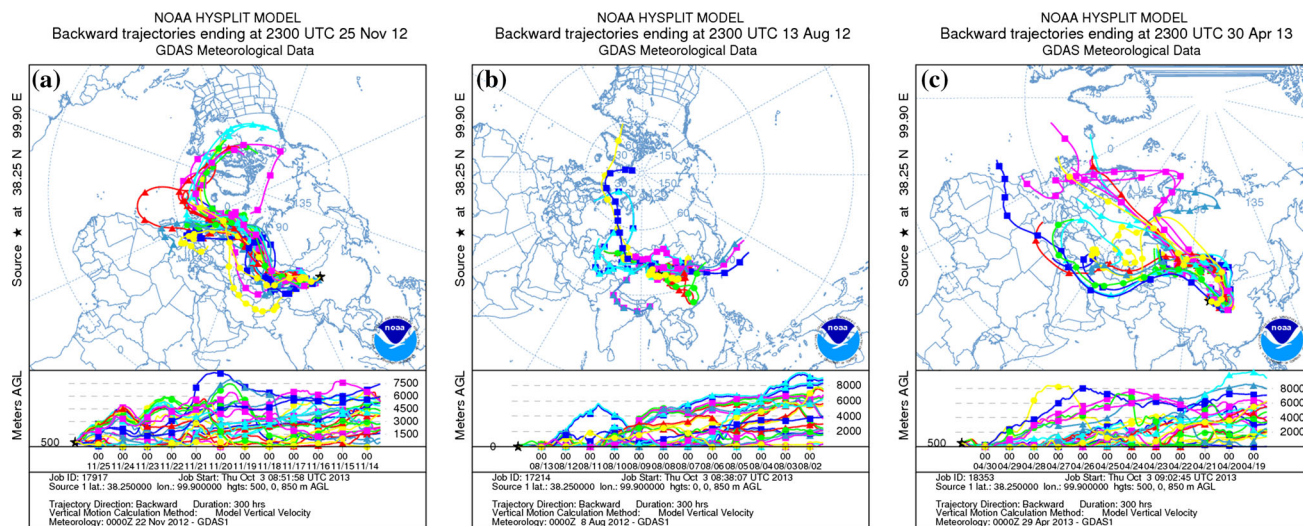

Fig. 8 Back trajectories of the air masses in 25 November 2012, 13 August 2012 and 30 April 2013
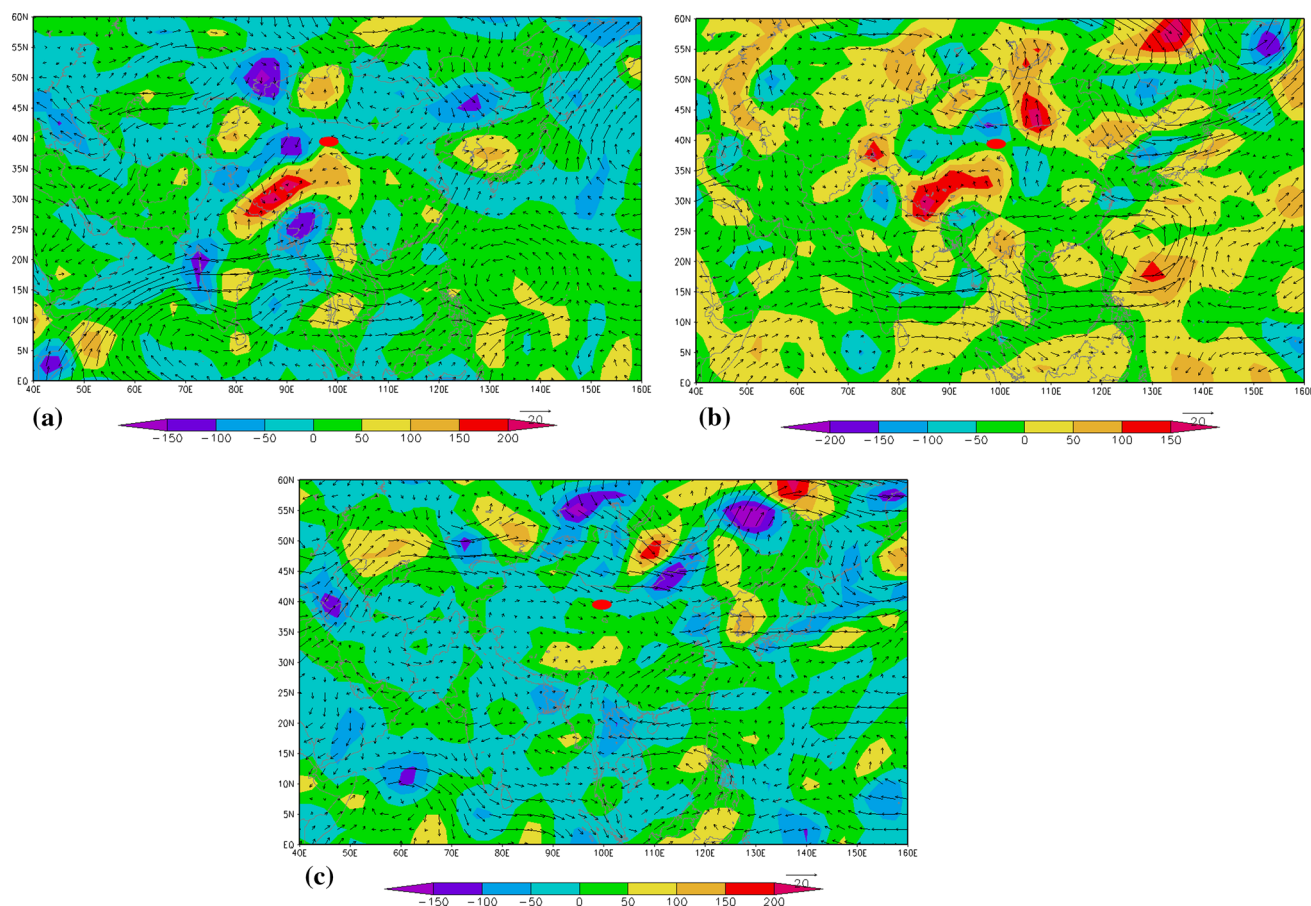

Fig. 9 The water vapor transportation vector in 13 August 2012 (taking as an example for monsoon precipitation events), 19 August 2013 (as an example for the interaction precipitation events) and 9 September 2013 (as an example for the westerly precipitation events) at 700 hPa (the *red tetragon* is Hulugou station)

Table 6 Comparison of major ions (μeq/L) and meteorological data for monsoon precipitation, the interaction precipitation and the westerly precipitation events

	Temperature (°C)	Relative humidity (%)	Precipitation (mm)	Wind speed (m/s)	Cl^-/Na^+	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
The monsoon precipitation events												
2012-8-10	12.90	83.23	5.60	3.50	0.52	20.23	81.97	30.62	38.86	5.90	8.45	44.19
2012-8-11	12.40	78.22	4.40	1.90	0.34	3.83	16.50	5.62	11.23	1.84	2.07	13.87
2012-8-12	12.10	84.07	20.10	2.30	0.48	5.90	8.74	6.27	12.17	1.75	2.21	16.11
2012-8-13	10.80	80.72	12.60	1.70	0.17	1.73	5.69	2.60	9.87	0.38	0.68	6.16
The interaction precipitation events												
2013-8-15	11.06	78.20	2.35	1.58	0.75	17.00	59.53	18.39	22.70	11.02	9.40	105.71
2013-8-16	7.07	87.88	8.55	1.30	0.85	17.94	46.52	13.90	21.13	3.79	20.55	156.68
2013-8-17	6.52	93.34	9.81	1.07	0.77	6.02	26.30	9.61	7.87	2.21	4.56	61.40
2013-8-18	11.47	81.05	15.91	1.06	1.07	8.21	23.95	7.25	7.70	16.52	2.84	25.11
2013-8-19	11.19	86.13	8.95	1.27	1.06	20.57	23.24	13.50	19.38	6.67	3.70	45.31
2013-8-20	10.38	86.50	2.77	1.00	1.38	18.42	18.68	19.75	13.35	3.67	6.80	69.56
2013-8-21	11.57	80.73	8.10	1.21	0.64	6.33	13.34	6.20	9.95	3.07	0.00	19.60
2013-8-22	10.71	87.96	9.01	0.96	0.81	5.71	7.64	6.34	7.05	1.87	0.00	25.34
2013-8-23	10.98	86.05	1.60	0.90	0.90	10.00	14.14	12.17	11.11	3.28	1.39	33.36
The westerly precipitation events												
2013-9-5	2.68	77.14	6.39	1.57	1.09	5.76	10.37	4.70	5.31	1.99	1.02	36.88
2013-9-6	4.81	66.83	5.60	1.82	1.20	33.50	11.03	2.11	27.98	45.24	20.28	55.58
2013-9-7	4.14	75.59	1.35	1.67	1.81	9.42	33.41	24.50	5.20	16.57	11.37	88.58
2013-9-8	4.14	68.39	0.40	1.80	2.34	26.81	56.59	33.70	11.47	15.91	17.43	131.31
2013-9-9	3.93	69.46	0.60	1.54	1.98	19.93	57.52	23.93	10.05	11.72	14.53	145.78

may be resulted in some influence from marine sources (Fig. 9).

To explore the influence from large-scale atmospheric circulation, the precipitation events can be divided into three types based on the water vapor transportation vector: the monsoon precipitation events, the interaction precipitation events (influenced both by monsoon and westerly) and the westerly precipitation events (Fig. 9). As shown in Table 6, the ionic concentration showed decreasing trend, and the composition ratio between the starting date and ending date for Cl^-, SO_4^{2-}, NO_3^-, Na^+, K^+, Mg^{2+} and Ca^{2+} is 0.09, 0.07, 0.09, 0.25, 0.06, 0.08 and 0.14, respectively, and precipitation and relative humidity had increased but temperature and wind speed decreased in the monsoon precipitation events. For the interaction precipitation events, chemical composition displayed the fluctuation from decrease to increase under the increasing temperature and relative humidity with the decreasing wind speed, while precipitation also firstly increased and then decreased. The composition of ending date for Cl^-, SO_4^{2-}, NO_3^-, Na^+, K^+, Mg^{2+} and Ca^{2+} is 3.46, 5.54, 5.09, 1.89, 5.90, 14.21 and 3.95 times higher than the starting date for the westerly precipitation events, respectively, while precipitation and relative humidity had decreased. So it can be deduced that the differences in precipitation chemistry

were partially due to the strength of the precipitation leaching under the different atmospheric circulation, which also made some influence on wet deposition in the central Qilian Mountains.

Comparison with other researches in neighboring regions

The mean concentrations of major ions in Hulugou basin compared with data from Tibetan Plateau, Brazil, India, Okinawa, Jordan, Turkey and other remote areas are presented in Table 7. Firstly, similar to our findings, Ca^{2+} and SO_4^{2-} in precipitation from Brazil, rural areas in India, Jordan, Okinawa, and Turkey accounted for the majority of the major ions. Therefore, the precipitation chemistry in these regions has a typical continental characteristics (Al-Khashman 2005) and partly anthropogenic disturbance (Jain et al. 2000; Ming et al. 2007). The higher Ca^{2+} and SO_4^{2-} in precipitation from study region may be due to the existence of CaSO4, similar to the scenario reported for Nam Co region, indicated by Li et al. (2007). To some extent, precipitation chemistry in the central Qilian Mountains is predominantly controlled by local/regional dusts. However, concentrations of all ions in precipitation at Hulugou basin are lower than those in precipitation from

Table 7 Major ion concentrations and conductivity (EC) at the central Qilian Mountains compared with other sites (ion concentration is in μeq/L,EC is in us/cm)

Study region	EC	Cl⁻	NO₃⁻	SO₄²⁻	Na⁺	K⁺	Mg²⁺	Ca²⁺
The central Qilian mountains	41.9	42	27.9	67.3	32.1	13.3	44.4	191.7
Yulong Mountains[k]	10.3	1.96	4.0	28.3	3.72	2.46	5.68	37.7
Central-TP[a]	19.7	19.2	10	15.5	18.1	14.5	7.43	301
Lhasa[b]		21.7	2	2.5	89	14.8	5.72	150
Brazil[c]	10.8	13.8	4	23.1	15.1	5.81	8.85	21.5
Tianshan[d]	31.3	0.52	0.4	1.9	0.98	0.16	3.42	16.3
Waliguan[e]	14.6	6.1	8.3	24	8.7	3.8	12.1	34
Okinawa[f]	34.8	188	14	25.8	180	10.6	37.4	22.2
Ru.India[g]		15.8	7.6	19.7	11.9	9.66	11.5	39.8
Jordan[h]	160	80.6	35.7	53.2	75.6	26.3	62.3	163.1
Turkey[i]	28.1	20.4	29.2	48	15.6	9.8	9.3	71.4
The eastern Qilian Mountains (Jiutiaoling)[j]		87.6	40.6	243.9	132.7	28.3	55.8	532

[a] Li et al. (2007), [b]Zhang et al. (2003b), [c]Migliavacca et al. (2005), [d]Dong et al. (2011), [e]Tang et al. (2000), [f]Mkadam et al. (2008), [g]Jain et al. (2000), [h]Al-Khashman (2005), [i]Topcu et al. (2002), [j]Ma et al. (2012), [k]Li et al. (2009b)

Jiutiaoling Station (the eastern Qilian Mountains).One cause for this may be that Hulugou basin is covered by alpine meadows, resulting in the weakening local sources relative to the region around Jiutiaoling. Secondly, it is interesting that ionic concentration in this study is higher than that of both Lhasa and Waliguan, which may be due to the existence of desert dusts as discussed above in Hexi corridor. Thirdly, it is obviously that the data from Hulugou station (3,260 m.a.s.l) are far lower than in Jiutiaoling because the effects of the continental dusts are weak at such high elevation (3,260 m) and all the ions have experienced heavy depletion in the former and, what is more, the Jiutiaoling is more nearby the dust source regions, located in the south of Tengger Desert. These comparisons further supported the conclusion that the precipitation chemistry in the central Qilian Mountains is predominantly controlled by local/regional dusts. When compared with precipitation chemistry studies from other remote areas, the concentrations of Ca²⁺ and SO₄²⁻ on Qilian Mountains are much higher due to both low precipitation and relatively large contributions of crustal aerosols. In addition, concentrations of sea salt ions (e.g., Cl⁻ and Na⁺) in Hulugou basin are also much higher than monsoonal climate region (Yulong Mountains, Okinawa), reflecting a weak contribution of sea salts on precipitation chemistry with long distance transport from the ocean.

Conclusions

The precipitation conductivity was controlled by alkaline earth elements ranging from 5.26 to 482 μs/cm with a mean value of 41.9 μs/cm in the central Qilian Mountains, and the high values were generally associated with winter and spring days, when sandstorm activities were also frequent. The average ionic concentrations for Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺ are 42, 67.3, 27.9, 32.1, 13.3, 44.4 and 191.7 μeq/L, and precipitation was of SO₄²⁻-Mg²⁺-Ca²⁺ type. Precipitation events occurred around summer displayed lower chemical concentrations, while it also had higher concentrations in winter and spring with little precipitation and larger wind speed. Although the precipitation in dry season only accounted for 3.1 % of total precipitation during the sampling period, the concentration for Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺ is 4.2, 5.93, 2.94, 1.47, 2.93, 2.11 and 3.79 times higher than that in wet season, respectively. The main ionic sources are local dust aerosols and the dust from central Asia and northwestern China arid regions brought by the westerly, and the back trajectories and water vapor transportation also supported it.

The non-sea sources played an important role in determining the ionic composition, and its contribution percentages for SO₄²⁻, K⁺, Mg²⁺ and Ca²⁺ were 99.8,97.4, 96.6 and 98.9 %, respectively. The precipitation events can be divided into three types: the monsoon precipitation, the interaction precipitation and the westerly precipitation events based on the water vapor transportation vector. For the first type, the ionic concentration showed the decreasing trend, and precipitation and relative humidity had increased but temperature and wind speed decreased. For the interaction precipitation events, chemical composition displayed the fluctuation from decrease to increase under the increasing temperature and relative humidity, and the decreasing wind speed. The composition of ending date is 3.46, 5.54, 5.09,1.89, 5.90,14.21 and 3.95 times higher than that of the starting date for Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺ in the westerly precipitation events, respectively, while precipitation and relative humidity had decreased. It can be concluded that the different atmospheric circulation also made some influence on wet deposition in the central Qilian Mountains.

References

Ali K, Momin GA, Tiwari S et al (2004) Fog and precipitation chemistry at Delhi, North India. Atmos Environ 38(25):4215–4222

Al-Khashman OA (2005) Ionic composition of wet precipitation in the Petra region, Jordan. Atmos Res 78(1–2):1–12

Asaf L, Nariv R, Hassan MA et al (2005) Influence of smalland large-scale variables on the chemical and isotopic composition of urban rainwater, as illustrated by a case study in Ashod, Israel. J Geophys Res 110:D11307. doi:10.1029/20045JD005414

Baron J, Denning AS (1993) The influence of mountain meteorology on precipitation chemistry at low and high elevations of the Colorado front range, USA. Atmos Environ 27A(15):2337–2349

Barras VJI, Simmonds I (2008) Synoptic controls upon d18O in southern Tasmanian episodic events. J Geophys Res 102(C12):2681–2687

Basak B, Alagha O (2004) The chemical composition of rainwater over Buyukcekmece Lake, Istanbul. Atmos Res 71(4):275–288

Calvo AI, Olmo FJ, Alados-Arboledas L et al (2010) Chemical composition of wet precipitation at the background EMEP station in Viznar (Granada, Spain) (2001–2006). Atmos Res 96:408–420

Celle-Jeanton H, Travi Y, Loÿe-Pilot M et al (2009) Rainwater chemistry at a Mediterranean inland station (Avignon, France): local contribution versus long-range supply. Atmos Res 91(1):118–126

Dong ZW, Li ZQ, Ross E et al (2011) Temporal characteristics of mineral dust particles in precipitation of Urumqi river valley in Tian Shan, China: a comparison ofalpine site and rural site. Atmos Res 101:294–306

Eneroth K, Holmén K, Berg T et al (2007) Springtime depletion of tropospheric ozone, gaseous elemental mercury and non-methane hydrocarbons in the European Arctic, and its relation to atmospheric transport. Atmos Environt 41:8511–8526

Fan HB, Hong W, Ma Z et al (1999) Acidity and chemistry of bulk precipitation, throughfall and stemflow in a Chinese fir plantation in Fujian, China. For Eco Manag 122:243–248

Feng Q, Liu W, Su YH et al (2004) Distribution and evolution of water chemistry in Heihe River basin. Environ Geol 45:947–956

Gibbs RJ (1970) Mechanisms controlling world water chemistry. Science 170:1088–1090

Hitchcock DR (1980) Sulphuric acid aerosols and HCl release in coastal atmosphere: evidence of rapid formation of sulphuric acid particulates. Atmos Environ 14:165–182

Hontoria C, Saa A, Almorox J et al (2003) The chemical composition of precipitation in Madrid. Wat Air Soil Poll 146:35–54

Huang YL, Wang YL, Zhang LP (2008) Long-term trend of chemical composition of wet atmospheric precipitation during 1986-2006 at Shenzhen City, China. Atmos Environ 42:3740–3750

Jain M, Kulshrestha UC, Sarkar AK et al (2000) Influence of crustal aerosols on wet deposition at urban and rural sites in India. Atmos Environ 34:5129–5137

Kalnay E (1996) The NCEP/NCAR 40-year reanalysis project. Bull Am Meteorol Soc 77:437–471

Kang S, Qin D, Mayewski PA et al (2002) Chemical composition of fresh snow on Xixabangma peak, Central Himalaya, during the summer monsoon season. J Glaciol 48(161):337–339

Kang S, Mayewski PA, Yan Y et al (2003) Dust records from three ice cores: relationships to spring atmospheric circulation over the Northern Hemisphere. Atmos Environ 37(34):4823–4835

Kang S, Mayewski PA, Qin D et al (2004) Seasonal differences in snow chemistry from the vicinity of Mt. Everest, central Himalayas. Atmos Environ 38(18):2819–2829

Kang S, Zhang Q, Kaspari S et al (2007a) Spatial and seasonal variations of elemental composition in Mt. Everest (Qomolangma) snow/firn. Atmos Environ 41(34):7208–7218

Kang S, Zhang Y, Qin D et al (2007b) Recent temperature increase recorded in an ice core in the source region of Yangtze river. Chin Sci Bull 52(6):825–831

Keene WC, Pszenny AP, Galloway JN et al (1986) Sea salt correction and interpretation of constituent ratios in marine precipitation. J Geophys Res 91:6647–6658

Kistler R, Kalnay E, Collins W et al (2001) The NCEP-NCAR 50-year reanalysis: monthly means CD-ROM and documentation. Bull Am Meteorol Soc 82:247–267

Lehmann CMB, Bowersox VC, Larson SM (2005) Spatial and temporal trends of precipitation chemistry in the United States, 1985–2002. Environ Pollut 135(3):347–361

Li CL, Kang SC, Zhang QG et al (2007) Major ionic composition of precipitation in the Nam Co region, Central Tibetan Plateau. Atmos Res 85:351–360

Li ZX, He YQ, Pang HX et al (2008) Source of major anions and cations of snowpacks in Hailuogou No.1 glacier, Mt.Gongga and Baishui glacier No. 1, Mt. Yulong, China. J Geogr Sci 14(1):115–125

Li ZX, He YQ, Pang HX et al (2009a) The chemistry of snow deposited during the summer monsoon and in the winter season at Baishui No. 1 Glacier, Mt Yulong, China. J Glaciol 55(190):221–228

Li ZX, He YQ, Pang HX et al (2009b) Environmental significance of snowpit chemistry in the typical monsoonal temperate glacier region, Baishui glacier No. 1, Mt.Yulong, China. Environ Geol 58:1319–1328

Li ZX, He YQ, An WL et al (2011) Climate and glacier change in southwestern China during the past several decades. Environ Res Lett 6(2011):045404

Li ZX, He YQ, Wang PY et al (2012) Changes of daily climate extremes in southwestern China during 1961–2008. Glob Planet Change 80–81(2012a):255–272

Ma JZ, Zhang P, Zhu GF (2012) The composition and distribution of chemicals and isotopes in precipitation in the Shiyang River system, northwestern, China. J Hydrol 436–437:92–101

Migliavacca D, Teixeira EC, Wiegand F et al (2005) Atmospheric precipitation and chemical composition of an urban site, Guaiba hydrographic basin, Brazil. Atmos Environ 39:1829–1844

Ming J, Zhang DQ, Kang SC et al (2007) Aerosol and fresh snow chemistry in the East Rongbuk Glacier on the northern slope of Mt. Qomolangma (Everest). J Geophys Res 112:D15307. doi:10.1029/2007/JD008618

Mphepya JN, Pienaar JJ, Galy-Lacaux C et al (2004) Precipitation chemistry in semi-arid areas of Southern Africa: a case study of a rural and an industrial site. J Atmos Chem 47(1):1–24

Okay C, Akkoyunlu BO, Tayanc M (2002) Composition of wet deposition in Kaynarca, Turkey. Environ Pollut 118:401–410

Rocha FR, Silva JAF, Lago CL et al (2003) Wet deposition and related atmospheric chemistry in the São Paulo Metropolis, Brazil: part 1. Major inorganic ions in rainwater as evaluated by capillary electrophoresis with contactless conductivity detection. Atmos Environ 37:105–115

Safai PD, Rao PSP, Momin GA et al (2004) Chemical composition of precipitation during 1984–2002 at Pune, India. Atmos Environ 38:1705–1714

Shrestha AB, Wake CP, Dibb JE (1997) Chemical composition of aerosol and snow in the high Himalaya during the summer monsoon season. Atmos Environ 31:2815–2826

Sickles JE II, Grimm JW (2003) Wet deposition from clouds and precipitation in three high-elevation regions of the Eastern United States. Atmos Environ 37:277–288

Tang A, Zhuang G, Wang Y et al (2005) The chemistry of precipitation and its relation to aerosol in Beijing. Atmos Environ 39:3397–3406

Theakstone WH (2011) A seven-year study of oxygen isotopes in daily precipitation at a site close to the Arctic Circle, Tustervatn, Norway: trajectory analysis and links with the North Atlantic Oscillation. Atmos Environ 45(2011):5101–5109

Tu J, Wang HS, Zhang ZF et al (2005) Trends in chemical composition ofprecipitation in Nanjing, China, during 1992–2003. Atmos Res 73:283–298

Vermette SJ, Drake JJ, Landsberger S (1988) Intra-urban precipitation quality: hamilton, Canada. Water Air Soil Pollut 38:37–53

Wang PY, Li ZQ, Gao WY et al (2011) Rapid shrinking of glaciers in the central Qilian Mt. Region of Northwest China, during the last 50 years. J Earth Sci 22(4):539–548

Wu JK, Ding YJ, Ye BS et al (2010) Spatio-temporal variation of stable isotopes in precipitation in the Heihe River Basin, Northwestern China. Environ Earth Sci 61:1123–1134

Yang Y, Chen RS, Song YX et al (2013) Measurement and estimation of grassland evapotranspiration in a mountainous region at the upper reach of Heihe River basin. China. Chinese. J Appli Eco 24(4):1055–1062 (in Chinese with English)

Zhang YH, Wu YQ (2007a) Characteristics of the δ18O in Precipitation in the Upper and Central Reaches of Heihe River. J Glaciol Geocryol 29(3):440–445 (in Chinese with English abstract)

Zhang YH, Wu YQ (2007b) Variation of δ18O in water in Heihe river basin. Adv Water Sci 18(6):864–870 (in Chinese with English abstract)

Zhang YH, Wu YQ (2009) Oxygen and hydrogen isotopes in precipitation in Heihe River basin, China. J Glaciol Geocryol 31(1):35–39 (in Chinese with English abstract)

Zhang DD, Jim CY, Peart MR et al (2003a) Rapid changes of precipitation pH inQinghai Province, the northeastern Tibetan Plateau. Sci Total Environ 305:241–248

Zhang DD, Peart M, Jim CY et al (2003b) Precipitation chemistry of Lhasa and other remote towns, Tibet. Atmos Environ 37:231–240

Zhang MY, Wang SJ, Wu FC et al (2007) Chemical compositions of wet precipitation and anthropogenic influences at a developing urban site in southeastern China. Atmos Res 84:311–322

Zhao Z, Tian L, Fischer E et al (2008) Study of chemical composition of precipitation at an alpine site and a rural site in the Urumqi River Valley, Eastern Tien Shan, China. Atmos Environ 42:8934–8942

Zhao LJ, Xiao HL, Dong ZB, et al. (2011) Origins of groundwater inferred from isotopic patterns of the Badain Jaran Desert, Northwestern China. Ground Water. doi:10.1111/j.1745-6584.2011.00895.x

Zimmermann F, Matschullat J, Bruggemann E et al (2006) Temporal and elevation-related variability in precipitation chemistry from 1993 to 2002, eastern Erzgebirge, Germany. Water Air Soil Pollut 170(1–4):123–141