

## Cloud and the corresponding precipitation chemistry in south China: Water-soluble components and pollution transport

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[1] To investigate the transport and deposition of pollutants in south China, the chemical composition of cloud water and rainwater was studied at Mount Heng, which is located in the heart of China's acid rain affected region. A total of 194 cloud samples and 38 event-based precipitation samples from March to May 2009 were analyzed for a wide variety of water-soluble compounds. The volume-weighted mean (VWM) pH of cloud water was 3.80, indicating an acidic nature. Compared with cloud water, precipitation was much less acidic with a VWM pH value of 4.35. The concentration results show that in cloud water,  $\text{SO}_4^{2-}$  was the dominant anion, followed by  $\text{NO}_3^-$ , controlling the acidity, while  $\text{NH}_4^+$  accounted for 69.8% of the total cations, dominating the cloud water neutralization. In rainwater, a similar situation appeared, but with a slightly higher  $\text{Ca}^{2+}$  concentration. In both cloud water and precipitation the acidities were found to be mainly due to sulfuric acid, followed by nitric acid. The calculation of neutralization factors and the application of multiple linear regression analysis showed the higher  $\text{NH}_4^+$  contribution to the neutralization process in both types of samples. The very weak correlations of ions in rain with the ones in cloud water on the event basis suggested that cloud and precipitation events may be associated with different air masses. With relatively high ionic concentrations and higher frequency, air masses from the east and south directions were associated with the high cloud deposition of the major species at our site.

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### 1. Introduction

[2] Acid deposition has been a serious environmental problem in East Asia for the last 2 decades. It is caused primarily by precursors of strong acids such as  $\text{SO}_2$  and  $\text{NO}_x$ . Substantial economic growth and increased energy consumption have resulted in increased anthropogenic emissions of air pollutants such as particulate matter (PM),  $\text{SO}_2$ , and  $\text{NO}_x$  in East Asia, especially in China. Ohara *et al.* [2007] estimated that over the period from 1980 to 2003, total energy consumption more than doubled in Asia, and anthropogenic emissions increased by 119% for  $\text{SO}_2$  and 176% for  $\text{NO}_x$ . Zhang *et al.* [2009] estimated that anthropogenic emissions in China increased by 36% for  $\text{SO}_2$ , 55% for  $\text{NO}_x$ , and 13% for PM from 2001 to 2006. As is known

to all, southern China has become the third region of the world to be seriously influenced by acid rain during the past several decades, joining northeast North America and central Europe. Acid precipitation has affected the rather considerable area in China, and the areas seriously influenced by acid deposition are located mainly in eastern, southern, and central China [Tang *et al.*, 2010].

[3] In high-elevation environments, cloud and fog liquid water have generally been recognized as being more acidic than rainwater [Herckes *et al.*, 2002; Sickles and Grimm, 2003; Beiderwieden *et al.*, 2005]. Cloud and fog droplets, which form in the lower layer of the troposphere where aerosols and gases are most abundant, act as a medium for various aqueous and gas phase chemical reactions. In general, cloud droplets are formed by water vapor condensation onto an aerosol particle which serves as a cloud condensation nucleus (CCN) [Raubert, 2003]. The chemical compositions of the particles acting as CCN determine the initial compositions of the cloud droplets, which can be further altered by the uptake of ambient gas and PM in the atmosphere. After the cloud droplets form, the size of the droplet further increases by subsequent water vapor condensation and collision and merger between droplets. When a cloud droplet becomes large enough to overcome the updrafts, the

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**Figure 1.** Location of Mount Heng and the distribution of precipitation acidity during 2008 in China. (Black and white plot: Currently, there are no applicable data about acid rain in Taiwan and the islands in the South China Sea.)

droplet begins to fall and precipitation is formed. As the drop falls, it can further take up water vapor and gaseous and aerosol species which will greatly influence the composition of the precipitation.

[4] While there have been many studies examining the chemical composition of acid deposition carried out worldwide [Aleksic *et al.*, 2009; Ali *et al.*, 2004; Das *et al.*, 2005; Négrel *et al.*, 2007; Safai *et al.*, 2004; Song and Gao, 2009], most of them have focused only on cloud water or precipitation. Even if some studies simultaneously collected cloud water and precipitation, there has been limited attention to the relationship between cloud water and rainwater. This paper presents for the first time the characteristics of cloud and rainwater collected during the spring (the annual rainy/foggy season for this region) at Mount Heng, a high-elevation site located in the humid and acid rain affected area of southeast China. The study on cloud and rainwater chemistry was part of a larger field campaign of a China National Basic Research Project at Mount Heng, which is aimed at the understanding the formation and transport of acidic substances and related pollutants. The purpose of this paper is to present and discuss the chemical characteristics of cloud and rainwater, to identify possible sources of the various components in both, and to propose the cause of acid deposition in the region. This study also reveals some aspects of the correlation between cloud and rainwater chemistry in this region, such as the ion contribution of cloud water to precipitation and the cloud droplets' role in rain events.

## 2. Experiments and Methodologies

### 2.1. Site Description

[5] As shown in Figure 1 [State Environmental Protection Administration (SEPA), 2009], Mount Heng is located in Hunan Province, about 500 km away from the East China Sea and South China Sea. The area has become one of the most heavily acid deposition-impacted areas in the world. Two of China's main industrial regions are located in

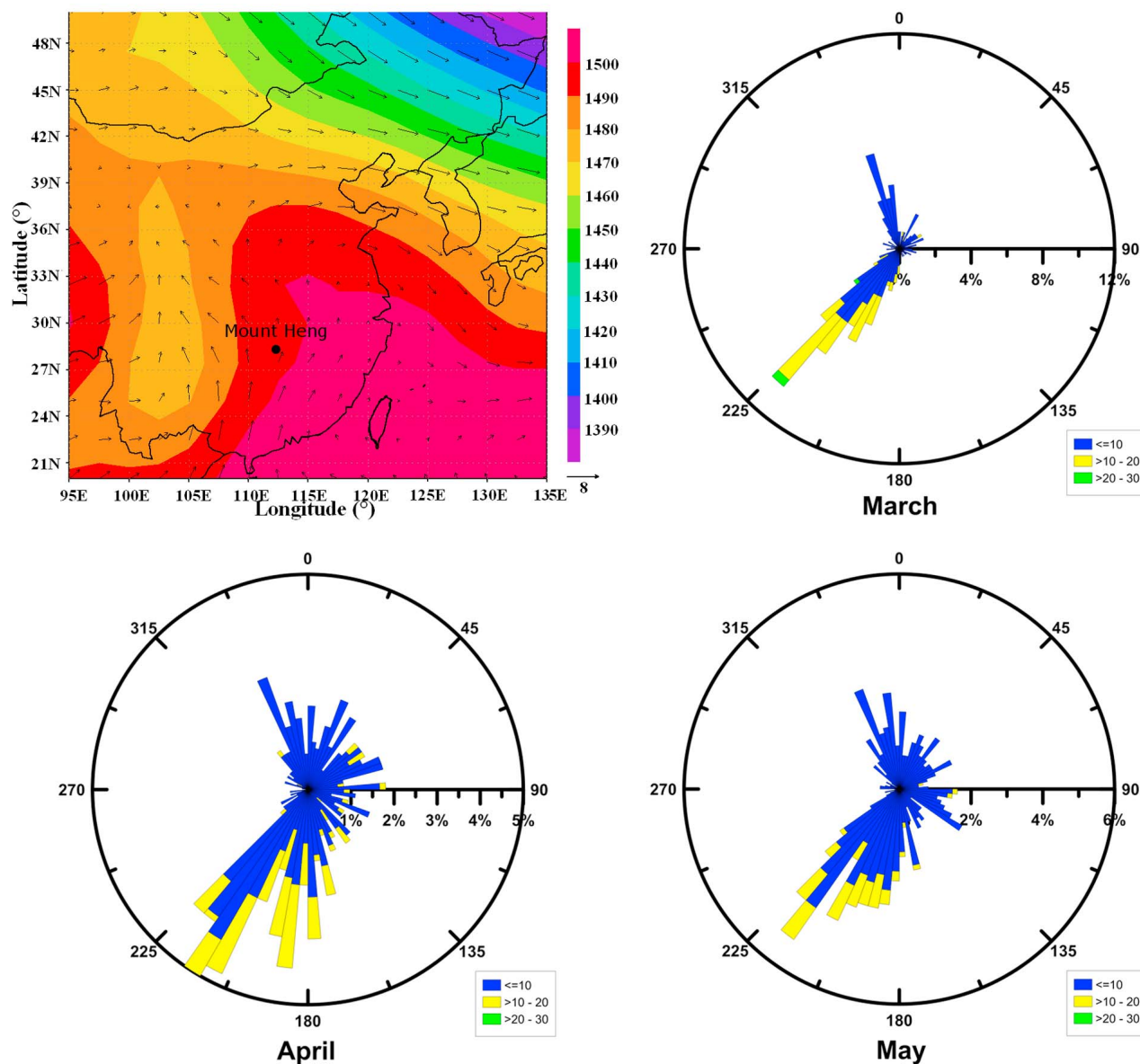
southern China, one centered on Shanghai and the other centered near Guangzhou; the study area is situated 900 km to the west and 400 km to north, respectively. Our monitoring site is in a meteorological station located at the summit of Mount Heng (27°18'N, 112°42'E, 1269 m a.s.l.). The local climate is characterized by four distinct seasons, high humidity, and abundant rainfall. Although the study area is less developed than the coastal areas of China, it has also experienced rapid growth for urbanization and industrialization in the recent 2 decades.

### 2.2. Meteorology

[6] The climate of southern China is strongly influenced by the Asian Monsoons [Ding, 1994; Fuelberg *et al.*, 2003]. Spring is the transitional period between the winter and summer. The Siberian High produces strong northeasterly winds in the planetary boundary layer. By March, the Siberian High weakens, while the Pacific High is building up. From March to May, the strength of the winter monsoon winds (characterized by cold and dry air masses) decreases, and the inflow of warmer and humid tropical air from the south becomes more frequent. The changes in large-scale airflow have been shown to have a significant impact on the variation of atmospheric constituents in coastal regions of southern China [e.g., Wang *et al.*, 2003]. Clouds are formed when cold and dry air from the north meets warm and humid air from the south. Figure 2 shows the mean geopotential height and vector winds at 850 hPa for March–May 2010 (NCEP reanalysis data). Analysis of the statistics of meteorological parameters from March to May 2009 (data from Mount Heng Meteorological Station) showed the mean monthly temperature increased from 9.8°C in March, to 12.2°C in April, and to 16.3°C in May. The amount of precipitation varied from 122 mm in March, to 231 mm in April, and 223 mm in May. Wind rose plots in Figure 2 show more frequent winds from the south.

### 2.3. Sample Collection

[7] All cloud-fog and rain events during the sampling period (from March to May 2009) were covered and a total of 194 cloud water samples and 38 rainwater event-based samples were collected during the monitoring period. Cloud water samples were collected using a Caltech active strand cloud water collector (CASCC) based on inertial impaction of each cloud droplet with a fan drawing air across three rows of Teflon strands. Rainwater samples were taken using a precleaned HDPE rain sampler with a diameter of 50 cm. Prior to each sampling, collectors were cleaned using Millipore water (18.2 MΩ resistivity), and all sample bottles were kept soaked in Millipore water for at least 24 h to avoid the influence of impurities. During cloud or rain events, samples were collected immediately until the whole event ended. The cloud event duration, precipitation volume, and other weather parameters for this sampling site were obtained from a nearby weather station at Mount Heng. After collection, samples were immediately transferred to the laboratory for analysis of electrical conductivity (EC) and pH. The samples were then filtered through 0.45 μm pore size membrane filters to remove insoluble particles, and preserved in a refrigerator under 4°C prior to chemical analysis.



**Figure 2.** Map showing 850 hPa mean geopotential height (unit: m) and wind vectors (unit: m/s) (using NCEP data), in combination with wind rose at Mount Heng (data from Mount Heng Meteorological Station) during the campaign.

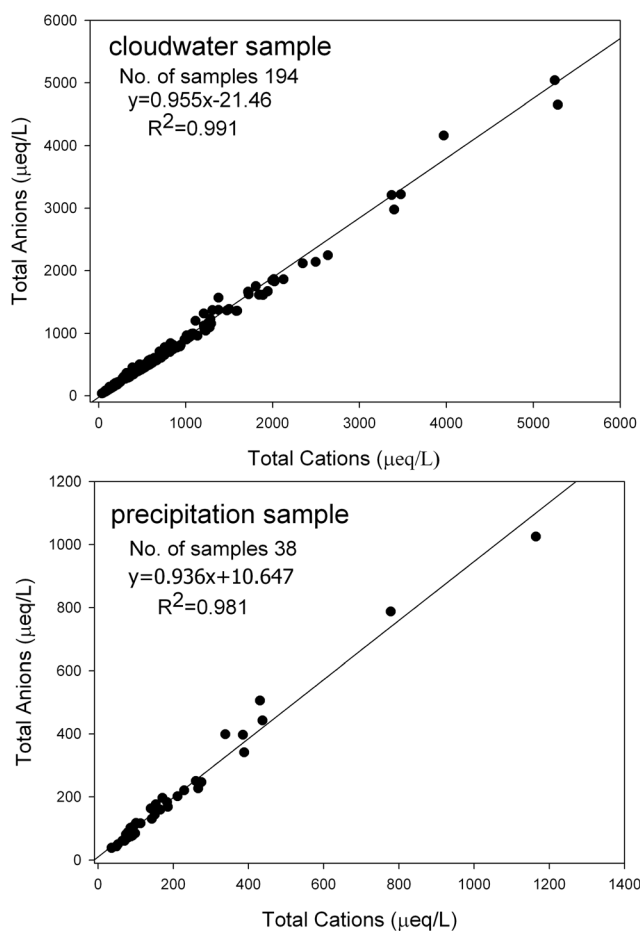
#### 2.4. Chemical Analysis

[8] Collected precipitation and cloud water samples were weighed and sample aliquots were taken for measurement of pH, EC,  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $NH_4^+$  and the organic acids (formate, acetate, oxalate, and lactate). The pH value and EC were measured using an autotitrator (MODEL 6350M, U.S.) in combination with the glass electrode (MODEL 106L, precision  $\pm 0.01$ ) with temperature compensation, in situ and in the laboratory. The pH meter was calibrated before each measurement using standard buffer solutions of pH 4.00 and 6.86. The measurement solution was 0.01 pH unit. The digital conductivity meter was periodically calibrated against KCl standard solutions. Samples of the inorganic ions and organic acidic species in

the cloud water and precipitation were analyzed by ion chromatography (Dionex, Model 2500) in the laboratory, which were completed within 1 day after samples were taken out from the freezer and thawed at room temperature.

#### 2.5. Quality Assurance and Control

[9] The collection and analysis of cloud water and precipitation samples were carried out according to the technical specifications from the USEPA (United States Environmental Protection Agency). Data quality of individual samples was checked by ion balance. The acceptable range for ion difference in samples, according to USEPA, is 15–30% for samples having ion concentrations of 100  $\mu\text{eq/L}$  [Rastogi and Sarin, 2005]. All the samples met the quality criteria



**Figure 3.** Electric charge equilibrium between total anions and total cations of cloud water and rainwater samples.

based on ionic balance. Strong linear correlation also existed between the two electrically charged groups of anions and cations with a slope of  $\sim 1.00$  ( $R^2 = 0.991$ ) (Figure 3), suggesting that good electric charge equilibrium existed between the two groups. Therefore the sampling and determination methods in the study are reliable.

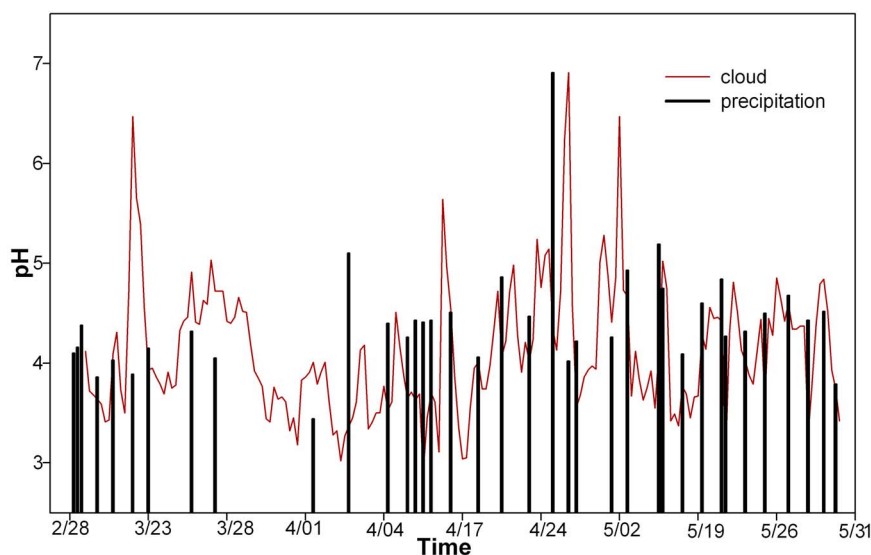
### 3. Result and Discussion

#### 3.1. The pH Value and Relative Ion Contributions of Clouds and Precipitation

##### 3.1.1. Variation of pH Value

[10] Figure 4 presents the temporal variation of pH values of cloud water and precipitation collected at Mount Heng in the period from March to May 2009. Similar pH ranges of cloud samples and individual rain events were observed (2.91 to 6.91 and 3.44 to 6.91) with volume-weighted mean (VWM) pH values 3.80 and 4.35, respectively. The naturally existing species  $\text{CO}_2$ ,  $\text{NO}_x$ , and  $\text{SO}_2$ , several organic acids and their precursors discharged by the flora and fauna could bring about a reduction in pH values of wet deposition in the clean environment to between 5 and 5.6 [Charlson and Rodhe, 1982; Galloway *et al.*, 1993]. Thus if pH values of samples are less than 5.0, this can indicate the influence of anthropogenic derived pollutants, while those with pH values more than 5.6 should absorb alkaline substances from the soil and anthropogenic sources. Of the cloud samples examined in this period, 92.7% exhibited  $\text{pH} < 5.0$ , while the corresponding percentage of the rain events was 92.1%, which suggests that the south is still one of the areas most seriously affected by acid deposition in China, and anthropogenic activities significantly impact the precipitation quality of this area.

[11] As shown in Figure 4, the highest pH values of cloud water and precipitation ( $\text{pH} 6.91$ ) were observed on the same day (24 April) when a huge sandstorm from the north had arrived at this location. There were multiple, apparently erratic peaks in cloud water acidity; whereas the most acidic



**Figure 4.** Time series of pH value of cloud water (red) and precipitation (black) from March to May 2009.

**Table 1.** Chemical Composition and pH in Spring Precipitation at Various Sites in the World ( $\mu\text{mol/L}$ )<sup>a</sup>

Site	Time	Altitude (m)	pH	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2+</sup>
This study	2009	1279	4.35	63.8	4.31	8.41	13.1	2.23	7.72	28.3	37.9
Mount Tai <sup>b</sup>	2006	1545	4.70	82.2	7.7	25.3	30.7	3.1	15.5	30.2	65.7
Happo, Japan <sup>c</sup>	2007	1850	4.80	25.0	1.40	5.10	11.7	1.97	6.67	18.6	23.6
Iraty, France <sup>d</sup>	2007	1300	5.15	0.32	0.05	0.62	0.14	0.04	1.00	0.23	0.18
Vorhegg, Austria <sup>d</sup>	2007	1020	5.56	0.36	0.04	0.11	0.14	0.03	0.21	0.29	0.15
Whiteface, New York <sup>e</sup>	2006	1483	4.75	10.3	0.6	0.6	1.7	0.5	1.0	8.7	10.5
Smith Valley, United States <sup>f</sup>	2008	1501	6.02	20.51	0.74	9.31	3.29	0.74	3.89	7.02	2.46
Canceta, United States <sup>f</sup>	2008	1057	6.21	30.94	1.28	4.74	13.00	1.68	3.50	15.47	12.25

<sup>a</sup>The statistics were calculated from the spring data sets which is the same period as our observation. According to altitude and distance from the seaside, the sites were selected from EANET in Asia, NADP in the United States, and EMEP in Europe. Site latitude, longitude and altitude for EANET, NADP and EMEP are available at [http://www.eanet.cc/product/datarep/datarep00/datarep00\\_intro.pdf](http://www.eanet.cc/product/datarep/datarep00/datarep00_intro.pdf), <http://nadp.sws.uiuc.edu/sites/latlong.asp>, and <http://tarantula.nilu.no/projects/ccn/network/index.html>, respectively.

<sup>b</sup>Wang *et al.* [2008].

<sup>c</sup>Network Center for EANET [2008].

<sup>d</sup>EMEP data set (2008).

<sup>e</sup>Aleksic *et al.* [2009].

<sup>f</sup>NADP data set (2009).

value measured in precipitation (pH 3.44) was clearly found on 1 April when the concentrations of alkaline species in the rainwater decreased sharply relative to acidic ions which was consistent with our observations. A fog event had lasted for several days before this rain event, which may have led to a reduction in particulate matter and the hourly PM<sub>10</sub> average concentration dropped from about 22.47  $\mu\text{g}/\text{m}^3$  when the fog began to occur to only 11.44  $\mu\text{g}/\text{m}^3$  after 6 days of fog, when the rain event occurred. On site measurements also indicated that acidic precursors such as SO<sub>2</sub> and NO<sub>x</sub> maintained a stable concentration in the ambient atmosphere in which the lowest pH in precipitation appeared (The data of PM<sub>10</sub>, SO<sub>2</sub> and NO<sub>x</sub> concentrations were provided by a parallel study group from the Environment Research Institute of Shandong University).

[12] The volume-weighted mean pH values of precipitation in this study and other sites in the world are shown in Table 1. The VWM pH value in this study was lower than that of Mount Tai which is located in northern China [Wang *et al.*, 2008]. Compared with observations in other high-elevation sites of the world, the mean acidity of rainwater was also much higher than those in sites located in East Asia [Network Center for EANET, 2008], Europe (EMEP acidifying/eutrophying compounds, 2008, [\[nilu.no/projects/ccn/onlinedata/main/monthly\\\_mean\\\_2008.dat\]\(http://tarantula.nilu.no/projects/ccn/onlinedata/main/monthly\_mean\_2008.dat\); hereafter EMEP data set, 2008\) and North America \[Aleksic \*et al.\*, 2009\] \(also National Atmospheric Deposition Program/NTN seasonal precipitation-weighted mean concentrations, 2009, <https://nadp.isws.illinois.edu/sites/ntnmap.asp?>; hereafter NADP data set, 2009\), suggesting that even compared to other sites greatly influenced by local industry, the area of southern China is one of the most serious acid rain zones in the world.](http://tarantula.</a></p>
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### 3.1.2. Compositions of Cloud and Precipitation and Relative Ion Contributions

[13] The VWM values of ion concentrations ( $\mu\text{mol/L}$ ) for cloud and precipitation in the overall period are listed in Table 2. The VWMs were used here in order to account for the effect of the precipitation amount on ion concentrations [Staelens *et al.*, 2005]. As shown in Table 2, the dominant ions were, both in cloud water and precipitation, sulfate, ammonium, nitrate, calcium, and sodium, which is similar to the results observed by previous studies in China [Hu *et al.*, 2005; Zhang *et al.*, 2007]. Also similar to prior researches [e.g., Bridges *et al.*, 2002; Aleksic *et al.*, 2009], these major ion concentrations were found to be much higher in cloud water than those in precipitation. There is a slight difference in ionic ratios between the two types of samples, in that these

**Table 2.** Volume-Weighted Mean Concentrations of Cloud and Precipitation Chemistry Parameters in the Overall Period

Species	Unit	Cloud			Number of Samples	Precipitation			Number of Samples
		Range	VWM	Ratio (%)		Range	VWM	Ratio (%)	
pH	-	2.91–6.91	3.80	-	193	3.44–6.91	4.35	-	38
EC	$\mu\text{s cm}^{-1}$	7.90–717.2	115.26	-	193	7.12–259.7	27.29	-	38
Na <sup>+</sup>	$\mu\text{mol L}^{-1}$	0.52–2199	66.03	5.8	193	0.87–95.66	8.41	3.2	38
NH <sub>4</sub> <sup>+</sup>	$\mu\text{mol L}^{-1}$	10.16–4081	356.47	31.2	193	9.61–413.5	63.76	24.5	38
K <sup>+</sup>	$\mu\text{mol L}^{-1}$	0.83–185.8	17.25	1.5	193	0.27–38.01	4.30	1.7	38
Mg <sup>2+</sup>	$\mu\text{mol L}^{-1}$	0.13–142.8	5.49	1.0	193	0.25–18.95	2.24	1.7	38
Ca <sup>2+</sup>	$\mu\text{mol L}^{-1}$	0.38–1363	29.83	5.2	193	1.44–125.1	13.03	10.0	38
F <sup>-</sup>	$\mu\text{mol L}^{-1}$	0.78–90.39	10.26	0.9	193	1.11–16.92	3.71	1.4	38
Cl <sup>-</sup>	$\mu\text{mol L}^{-1}$	0.66–410.1	21.07	1.8	193	1.55–75.12	7.72	3.0	38
NO <sub>2</sub> <sup>-</sup>	$\mu\text{mol L}^{-1}$	Nd–3.24	0.60	0.1	193	ND–1.50	0.07	-	38
NO <sub>3</sub> <sup>-</sup>	$\mu\text{mol L}^{-1}$	4.39–2528	158.80	13.9	193	5.44–267.9	28.34	10.9	38
SO <sub>4</sub> <sup>2-</sup>	$\mu\text{mol L}^{-1}$	9.85–1810	196.39	34.3	193	0.86–308.7	37.97	29.2	38
Formate	$\mu\text{mol L}^{-1}$	0.91–134.16	19.65	1.7	193	1.34–51.48	14.30	5.5	38
Acetate	$\mu\text{mol L}^{-1}$	0.60–185.79	16.04	1.4	193	1.10–104.7	16.04	6.3	38
Oxalate	$\mu\text{mol L}^{-1}$	0.19–62.70	5.11	0.9	193	0.27–11.13	1.65	1.3	38
Lactate	$\mu\text{mol L}^{-1}$	0.13–86.24	3.41	0.3	193	0.29–31.25	2.92	1.3	38

**Table 3.** Summary of Fractional Acidity and Neutralization Factors of Ammonium, Calcium, and Sodium

		Contribution of Acidic Ions			Neutralization of Alkaline Species (NF)		Fractional Acidity
		Sulfate	Nitrate	Organic Acid	Ammonium	Calcium	
Cloud	Range	0.27–0.83	0.06–0.51	0.018–0.37	0.01–1.04	0.001–0.59	0.001–0.87
	Average	0.71	0.25	0.04	0.61	0.11	0.28
	VWM	0.69	0.27	0.04	0.62	0.10	0.28
Rain	Range	0.05–0.69	0.07–0.34	0.09–0.74	0.12–1.06	0.04–0.46	0.001–1.66
	Average	0.60	0.21	0.19	0.51	0.22	0.33
	VWM	0.61	0.22	0.17	0.51	0.21	0.35

five dominant ions contributed 90% to the cloud total ionic content (TIC) versus 77% for precipitation. Their relative contributions to TIC calculated are as follows. Sulfate and nitrate contributions to TIC were about the same in cloud and rainwater, but ammonium and sodium contributed 37% to cloud water TIC versus 28% for rainwater. This was roughly compensated by opposite differences in calcium TIC contributions. Sulfate was the highest concentration anion in both types of samples due to the fact that coal is still the major energy source in China. The high percentages of ammonium ions, which are mainly noncrystal in origin, in both cloud water and precipitation, indicates a high anthropogenic contribution to ammonium ions in the study area.

[14] In addition to the aforementioned major ions, minor ions including five additional inorganic and six organic acids contributed only a few percent of the total ionic content. As in the case of the major ions, the minor ions also exhibited higher concentrations in cloud water than in precipitation (Table 2). The contribution of organic acids to TIC in rainwater was found to be much higher than that for cloud water (14.4% versus 4.4%). This result is due to the fact that the VWM concentrations of organic acids in cloud and precipitation were almost the same relative to the great difference of TIC. Compared with the great dilution of inorganic ions between cloud and precipitation, the differences in VWM concentrations of the organic acids were very slight. According to a previous finding [Song and Gao, 2009], a weak concentration dilution effect on organic acids can produce this slight difference between the concentrations.

[15] We compared the VWM concentrations of chemical species in precipitation measured at Mount Heng with those at other high-elevation locations (see Table 1). The TIC of precipitation in this study was only lower than that found at Mount Tai, which is greatly influenced by anthropogenic activities in the North China Plain and periodic sandstorms [Wang et al., 2008]. Although the input of acidic ions is very large in the northern areas, rainfall in the north contains a large number of alkaline species, while precipitation of the south has much lower levels of these species which results in the high acidity of rainwater in this area. Compared to data from other global sites [Network Center for EANET, 2008; Aleksic et al., 2009] (also EMEP data set, 2008, and NADP data set, 2009), the TICs of the rain in both locations in China are much higher, even though the other sites are also located near industrial zones. Thus the acidity measured in this study was due not only to a lack of alkaline substances to neutralize the acidity of precipitation, but also to a large contribution by acidic ions. In this site the concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  impacted by anthro-

pogenic activities were much higher than those reported for Europe, North America, and East Asia. The concentrations of minor ions such as  $\text{K}^+$  and  $\text{Mg}^{2+}$  were slightly higher than those at the other global sites. The contents of marine elements ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) were close to those found in Japan and the Smith Valley (both located near the sea). The level of calcium was close to levels found in Japan and Canceta, which are both influenced by spring sandstorms, but was slightly higher than values reported at other high-elevation locations.

### 3.2. Quantification of Acidifying and Neutralizing Potentials

[16] The acidity in precipitation found in this study was much higher compared with the available data from other locations in China and the world and demonstrated significant “acid rain” characteristics in the study zone. Given this situation, we analyzed for total free acidity (TFA) and neutralization of precipitation and its precursor “cloud fog.”

[17] To evaluate the contribution of acids to the acidity of wet deposition, we analyze the total free acidity (TFA) which was introduced by Keene et al. [1983]. TFA is associated with the definition, the amount of hydrogen ion in the free state, which is considered to be suitable to analyze in the solution acids, especially weak acids. We calculated the free hydrogen ion concentration provided by weak acids based on the measured concentrations of weak acids and the dissociation constants of selected species. As shown in Table 3, sulfate contributed in excess of 60% of the acidity, followed by the contribution of nitrate (more than 20%), while organic acids contributed 4% to cloud water TFA versus 17% for rainwater TFA. These results suggest that the acidity was caused mainly by sulfate and nitrate, while organic acids cannot be ignored as contributors to the acidity in the precipitation. In general, wet deposition acidity is due mainly to  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , while HCl, HF, and organic acids generally contribute negligibly to acidity [Khawaja and Husain, 1990]. In contrast to previous work, this study found organic acids to be major additional contributors to acidic precipitation. The finding fits with the prediction from Keene et al. [1986] that organic acids may account for about 15% of the total rainwater acidity in North America.

[18] To better understand the acidity of cloud water and precipitation, fractional acidity (FA) [Balasubramanian et al., 2001; Tuncer et al., 2001] was used to measure the acid neutralization state in wet deposition. Considering that organic acids were major extra contributors to the acidity and could not release all hydrogen ions as weak acids, we improved the original FA method by adding an organic acid

**Table 4.** Multiple Linear Regression Data for Sulfate and Nitrate Against Ammonium, Calcium, Sodium, and Hydrogen

Independent Variables	Cloud	Precipitation
Sulfate		
Explained by ammonium (%)	53.6	61.6
Explained by calcium (%)	25.8	18.6
Explained by hydrogen (%)	21.2	20.3
Nitrate		
Explained by ammonium (%)	46.3	52.7
Explained by calcium (%)	37.3	31.2
Explained by hydrogen (%)	15.1	16.1

component in the free state. If the ratio (FA) is at unity, it is considered that the acidity generated by these acids is not neutralized at all; when the FA value is zero, it is thought that all acids have been neutralized by alkaline substances. In our case, the average ratio values were 0.28 and 0.35 for cloud water and rain (Table 3), which means that 72% and 65% of the acidities were neutralized by alkaline substances over the entire study period. From the comparison, the acid neutralization state in cloud water was found to be higher than that in precipitation, owing to the fact that fog events generally preceded the reduction in alkaline particles brought about by associated rain events. In addition, the higher proportion of weak acids, such as organic acids, present in precipitation compared to that in cloud water caused the rain to have a stronger acidic buffering capacity, which decreased the influence of alkaline substances on acidity.

[19] We also compared the acid neutralization states in this study with those in a previous study [Wang *et al.*, 2008], and found that in spring the pH of cloud water at Mount Heng was basically the same as that at a high-elevation site, Mount Tai in North China (pH 3.80 versus 3.81), whereas the acidity of precipitation at Mount Heng was much higher than that at Mount Tai (pH 4.35 versus 4.68). The more acidic rainfall in the south could be explained by the fact that particulate matter over the southern areas has much weaker acidic buffering capacity compared with the northern areas [e.g., Wang and Wang, 1996; W. Wang *et al.*, 2006].

[20] In order to measure the contribution of the total alkaline species to the neutralization process, the neutralization factor (NF) was calculated according to the equation proposed by Possanzini *et al.* [1988] and Kulshrestha *et al.* [1995]. At Mount Heng, neutralization in both cloud water and rain was produced mainly by ammonium (more than half the total effect), while calcium contributed slightly about 20% of the neutralization (Table 3). These results support the view that neutralization is primarily caused by anthropogenic  $\text{NH}_3$  [Zunckel *et al.*, 2003], while airborne particulate  $\text{CaCO}_3$  is also a major factor [Al-Momani, 2003].

[21] Multiple linear regression (MLR) analysis was used to assess the relationship between the concentrations of anions  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and the cations  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$  and  $\text{H}^+$  as independent variables according to the equations provided by Anatolaki and Tsiouridou [2009]. Table 4 shows MLR data between  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and the cations  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{H}^+$  for cloud-fog samples and rain event-based samples. The results shown in Table 4 suggest that ammonium is the major neutralizing agent for both sulfate and nitrate in cloud water and precipitation, with the contribution accounting for

about half of the neutralization. Calcium also plays a significant role in the neutralization process, and the neutralization contribution to cloud water is higher than that in rainwater. According to their associations with  $\text{H}^+$ , the amounts of sulfate and nitrate in cloud water and rain that were not neutralized by alkaline species were otherwise about the same. However, the acid neutralization state in precipitation was lower than that in cloud water, due solely to organic acids being left out of the MLR analysis.

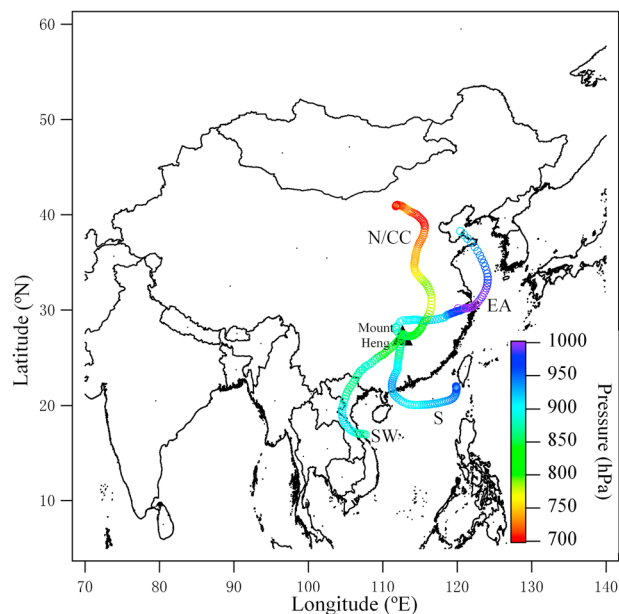
### 3.3. Relationships Between Ions

[22] In order to study the ion behavior from cloud to precipitation, the cloud and precipitation chemistry was compared for an event basis. We first averaged cloud water ion concentrations for a cloud-fog event. The averages for cloud water were then matched to the concentrations of rainwater collected at a very close time period. It is found that 26 precipitation samples and the corresponding event-based cloud-fog averages could match each other. The correlation coefficients based on intercomparison of the measured ion concentrations on an event basis are shown in Table 5. Analysis of matched pairs did not show any strong relationship between cloud and rain chemistry and correlations between cloud water and precipitation ions were low in the range  $-0.350$  to  $0.467$ . The lack of correlation suggests that the cloud and precipitation events may be associated with different air masses. Also the weak relationship between cloud water and precipitation chemistry may be due to the fact that the rain formed from a different cloud from the one that was sampled: precipitating versus non-precipitating clouds [Aleksic *et al.*, 2009].

[23] Besides correlation coefficients based on intercomparison of cloud with precipitation, Table 5 also lists the ones based on intracomparison on the sample basis. Note that while there is a high degree of correlation between the

**Table 5.** Intracorrelation and Intercorrelations Between Ions for Cloud Water and Precipitation

	Correlations for Rain Ions				
	$\text{NH}_4^+$ -Rain	$\text{Ca}^{2+}$ -Rain	$\text{Na}^+$ -Rain	$\text{NO}_3^-$ -Rain	$\text{SO}_4^{2-}$ -Rain
$\text{NH}_4^+$ -rain	1				
$\text{Ca}^{2+}$ -rain	0.686	1			
$\text{Na}^+$ -rain	0.328	0.542	1		
$\text{NO}_3^-$ -rain	0.934	0.789	0.290	1	
$\text{SO}_4^{2-}$ -rain	0.978	0.746	0.304	0.970	1
	Correlations for Ions of Cloud Water				
	$\text{NH}_4^+$ -Cloud	$\text{Ca}^{2+}$ -Cloud	$\text{Na}^+$ -Cloud	$\text{NO}_3^-$ -Cloud	$\text{SO}_4^{2-}$ -Cloud
$\text{NH}_4^+$ -cloud	1				
$\text{Ca}^{2+}$ -cloud	0.592	1			
$\text{Na}^+$ -cloud	0.488	0.355	1		
$\text{NO}_3^-$ -cloud	0.900	0.779	0.535	1	
$\text{SO}_4^{2-}$ -cloud	0.931	0.640	0.672	0.899	1
	Correlations Between Cloud and Rain Ions				
	$\text{NH}_4^+$ -Rain	$\text{Ca}^{2+}$ -Rain	$\text{Na}^+$ -Rain	$\text{NO}_3^-$ -Rain	$\text{SO}_4^{2-}$ -Rain
$\text{NH}_4^+$ -cloud	0.214	0.017	-0.335	0.079	0.134
$\text{Ca}^{2+}$ -cloud	0.194	0.467	0.013	0.134	0.166
$\text{Na}^+$ -cloud	-0.104	0.017	-0.056	-0.018	-0.087
$\text{NO}_3^-$ -cloud	0.227	0.219	-0.249	0.220	0.212
$\text{SO}_4^{2-}$ -cloud	0.135	0.044	-0.350	0.037	0.082

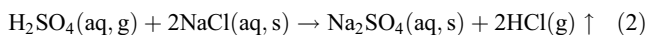
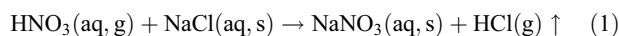


**Figure 5.** Typical pathway of each trajectory category.

major ions (aside from sodium) on an intrabasis for both cloud water and precipitation, this is not the case between cloud water and precipitation.

[24] In both cloud water and precipitation,  $\text{NH}_4^+$  showed very good correlations with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , suggesting that ammonia generally occurs in the atmosphere as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ , and  $\text{NH}_4\text{NO}_3$  aerosols by reacting with sulfuric acid and nitric acid [Bridgman, 1994; Seinfeld, 1986; Zhang *et al.*, 2007]. In rainwater,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  correlated highly with each other, which may be attributable to the similarity of their chemical behaviors in precipitation and of their precursors  $\text{SO}_2$  and  $\text{NO}_x$ . Correlation coefficients of  $\text{Ca}^{2+}$  versus  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were both lower than those of  $\text{NH}_4^+$  versus  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , showing that  $\text{NH}_4\text{HSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{NH}_4\text{NO}_3$  could be more predominant than  $\text{CaSO}_4$  and  $\text{Ca}(\text{NO}_3)_2$  in the atmosphere [Ali *et al.*, 2004]. Similar results were also obtained on the basis of correlations for ions of cloud water, suggesting that ions in cloud water also show similar chemical behaviors.

[25]  $\text{Na}^+$  ion levels did not correlate highly with  $\text{NH}_4^+$  and  $\text{Ca}^{2+}$ , the two major ions in cloud water and precipitation, implying that the source of sodium is very different from those of the other dominant ions. It is worth noting that  $\text{Na}^+$  showed a much higher correlation with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  within cloud water than within precipitation. The difference may be due to such a fact. In nonprecipitating clouds collected, sea salt aerosols as CCN may react with acids such as nitric and sulfuric acids, and thereby lose chloride ions according to reactions 1 and 2 [Zhuang *et al.*, 1999].



And yet this case did not occur in precipitating clouds, leading to a weak relationship between  $\text{Na}^+$  and  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  in rainwater. This is partly borne out by the greater Cl loss in clouds compared to that in precipitation.

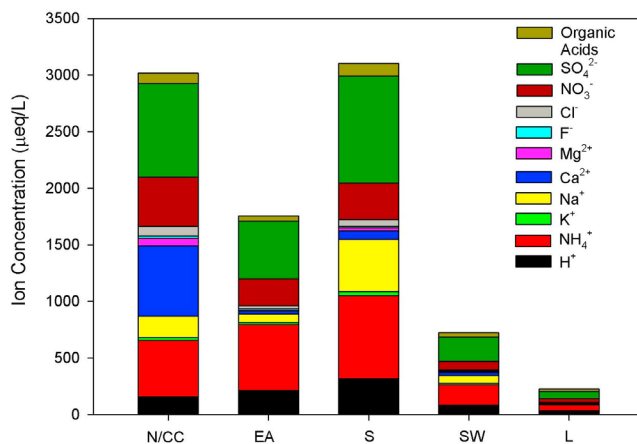
### 3.4. Local Contribution and Long-Range Transport

[26] To characterize the source-cloud event relationships, back trajectory analysis was conducted. This kind of study has been adopted in many acid deposition studies [Wang *et al.*, 2008; Song and Gao, 2009] and the method has proven to be effective in identifying the source region for pollutants measured in a receptor. The air mass back trajectories were calculated using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model, employing archived NOAA global reanalysis meteorological data. Cloud event times were put into the NOAA HYSPPLIT model to generate 5 day back trajectories in sets of three for arrival heights at 1000 m, 1265 m and 1600 m a.s.l for a vertical cross section of the atmosphere.

[27] A cluster analysis of the trajectories using the statistical software SPSS was undertaken to determine the significant transport patterns influencing cloud water chemistry. For the cluster analysis we selected cases in which the trajectories at the above three elevations came from the same direction. Each trajectory set comprised coordinate pairs (longitude, latitude and height) at the 4 h resolution for the previous 5 days as the clustering variables. Within a total of 90 variables ( $3 \times 6 \times 5$ ), about 100 back trajectories were segregated into clusters using Ward's method to compute the square Euclidean distances between trajectory sets by K-mean clustering technique. This clustering method is commonly used in other studies [Gao and Anderson, 2001; T. Wang *et al.*, 2006].

[28] The typical pathway of each trajectory category is shown in Figure 5. The cloud-fog events are classified into five major categories: N/CC, continental air masses from northern and central China with the frequency 10%; EA, air masses from the eastern industrial area centered around Shanghai (the frequency is 29%); S, air masses from the South China Sea which then transversed the Pearl River Delta region, one of the most industrially developed areas in China (the frequency is 33%); SW, air masses from Southeast Asia with the frequency 13%; and L, samples with looped trajectories that remained within a radius of 200 km of our site with the frequency 15%.

[29] Figure 6 shows the VWM ion concentrations determined for each of the five defined sectors. The categories



**Figure 6.** VWM species concentrations based on different trajectory categories.



EA and S represent the predominant air mass origin with greater amounts of cloud water and more frequent occurrence. Although the TICs of the N/CC category were much higher than those in the other categories, except category S, the main contributors to total cloud deposition flux were air masses from the east and south. The air masses of the N/CC group originate from north China and even more from northern Mongolia where desert and loess regions are located, so the cloud water of this group is characterized by elevated  $\text{Ca}^{2+}$  concentrations (621.9  $\mu\text{eq/L}$ , a concentration second only to that of  $\text{SO}_4^{2-}$ ) and the lowest  $\text{H}^+$  ratio. The low  $\text{Na}^+$  ratio of this group supports the fact that the samples are of continental origins. The cloud water in the EA category was moderately acidic and inferior only to that in the S category. In this category, the low ratios of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  to TIC indicate that the components of air masses from this direction were little influenced by terrestrial and marine sources. The high  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  ratios are consistent with the emission sources over this region: intensive agriculture, developed industry, and busy traffic. The cloud water in the S category was most acidic, with the highest  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , but low  $\text{Ca}^{2+}$  concentrations. It is worth noting that the  $\text{NH}_4^+$  concentration in this group was also highest in these clusters, but this did not prevent acidification of the cloud water. In addition, the marine tracer  $\text{Na}^+$  concentration was much higher than in the other categories. The air masses belonging to category SW and L were much cleaner than those of the three categories mentioned above. The  $\text{H}^+$  concentrations in these two groups were the lowest two values observed due to lower input of acidic ions with air masses.

#### 4. Summary and Conclusions

[30] An investigation of cloud water and precipitation chemistry was carried out in the central area of southern China from March to May of 2009. The cloud water and precipitation were typically acidic as similar pH ranges of cloud samples and individual rain events were observed (2.91 to 6.91 and 3.44 to 6.91, respectively).

[31] In cloud water and precipitation the dominant anions were sulfate and nitrate, while the dominant cations were ammonium, calcium, and sodium. These five major ions contributed 90% to cloud TIC versus 77% for that of precipitation, and their concentrations were much higher in cloud water than in rainwater for all ions. Even though the concentrations of sulfate and nitrate were not high relative to that in the northern areas of China, rainwater in the study area was typically acidic due to poor neutralization.

[32] The acidities in cloud water and precipitation were caused mainly by sulfate, with nitrate and organic acids appearing as additional acidity contributors. The calculation of neutralization factors (NFs) and the application of multiple linear regression (MLR) analysis showed the higher  $\text{NH}_4^+$  contribution to the neutralization process in both types of samples.

[33] The concentrations of major ions except sodium on the sample basis tracked each other within cloud water and within precipitation. However, concentrations in cloud water did not correlate those in precipitation, and thus rainwater measurements are not a good substitute for cloud chemistry measurements.

[34] The coupling between the information provided by the chemical content and air mass back trajectories highlights the importance of the origin of air masses in the acquisition of cloud water chemistry. Highest primary ionic concentrations were associated with N/CC air mass cluster, which passed over the heavily polluted areas of central China, while the lowest pollutant concentrations were associated with the local air mass cluster, which is consistent with the undeveloped nature of the region. The S category was associated with the highest acidity, which could be explained by anthropogenic sources influencing the composition of air masses from southern China, and the L category was associated with the lowest acidity. The air masses that passed over continental Asia were characterized by the highest concentration of crust tracer  $\text{Ca}^{2+}$ , while the highest concentration of marine tracer  $\text{Na}^+$  was associated with the southerly air mass cluster, the air of which spent most of its time over the South China Sea.

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