Characterization of cloud water chemistry at Mount Tai, China: Seasonal variation, anthropogenic impact, and cloud processing

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HIGHLIGHTS

► A comprehensive study of cloud water was conducted at Mt Tai in China in 2007–2008.
► Cloud water composition at Mt. Tai is strongly influenced by anthropogenic emissions.
► Cloud water has low pH values and is more acidic for air masses from southern China.
► Drop-size dependence of cloud ionic composition varies with cloud evolution.
► In-cloud S(IV) oxidation on average accounts for 27% of the total cloud sulfate.

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ABSTRACT

To investigate cloud chemistry in the fast developing region of north China, five intensive observation campaigns were performed at the summit of Mount Tai (Mt. Tai) during 2007–2008. A total of 482 cloud water samples were collected using single-stage and two-stage cloud collectors. Inorganic ions, organic acids and species associated with S(IV) oxidation in cloud water were analyzed. The results showed that 80% of the cloud samples were acidic (pH $<$ 5.6), and 55% of the samples were strongly acidified (pH $<$ 4.5). The clouds at Mt. Tai contained much higher anthropogenic and crustal ion concentrations than observed at many other rural sites; the most abundant ions in the cloud water were NH_4^+ (volume weighted mean concentration of 1215 μeq L^{-1}), SO_4^{2-} (1064 μeq L^{-1}), NO_3^- (407 μeq L^{-1}) and Ca^{2+} (193 μeq L^{-1}), suggesting large influences of anthropogenic emissions on cloud water. Seasonal variations of cloud composition were observed, showing high fractions of NH_4^+ and SO_4^{2-} in summer and more soil/ crustal ions in spring and winter. Backward trajectory analysis showed that the cloud water pH in air masses arriving from the south was typically much lower than when air was transported from the north. Higher nitrate fraction and low pH were found in air masses from the industrialized coastal regions of China, indicating an increased contribution of HNO_3 to cloud acidification due to higher NO_x emissions. The drop size dependence of cloud chemical composition was examined. Smaller droplets were more acidified than larger ones. The drop size dependence tendency of ion concentrations varied with cloud evolution. SO_4^{2-}, NH_4^+ and NO_3^- were more enriched in larger droplets in the initial stages of the clouds, and tended to be higher in smaller drops with cloud development. In-cloud aqueous sulfate formation was estimated using a selenium tracer method. In-cloud aqueous production on average accounted for 27% of the measured cloud water sulfate, with a range from 5% to 62% for individual cloud events.

1. Introduction

Clouds can cover more than 50% of the Earth's surface area at any given time, and are important elements of the atmospheric system (Ravishankara, 1997). Clouds play a key role in determining the Earth's radiation budget and directly or indirectly affect

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climate; they are also important for the transport and redistribution of atmospheric constituents (Seinfeld and Pandis, 2006). Clouds can scavenge gases and particles and produce secondary inorganic/organic species through aqueous-phase reactions (Anderson et al., 1999; Ghan et al., 1998). In-cloud formation has been suggested to be responsible for more than 80% of the atmospheric sulfate produced from SO_2 (Langner and Rodhe, 1991).

Many researchers have investigated cloud chemical composition, droplet formation processes, interactions between aerosols, soluble gases and clouds, and aqueous-phase reactions in cloud droplets (Collett et al., 2002; Fahey et al., 2005; Herrmann et al., 2005a). The initial physical and chemical properties of the cloud droplets depend on the size and chemical composition of cloud condensation nuclei (CCN) and also the supersaturation of ambient water vapor. During the evolution of the cloud, the scavenging of soluble gases and non-activated aerosols, aqueous-phase reactions, and meteorological conditions can greatly influence the physical–chemical characteristics of the cloud (Fuzzi et al., 2001; Kelly et al., 2007; Tilgner et al., 2005). Due to the underlying variation in CCN composition with particle size and the dependence of a variety of processes (e.g., condensational growth, soluble gas dissolution) on drop size, variations in solute concentration with droplet size have been predicted and observed in many locations (e.g., Bator and Collett, 1997; Kelly et al., 2007; Moore et al., 2004; Ogren et al., 1992; Reilly et al., 2001).

The characteristics of cloud water have been observed in various regions of the world. Motivated by interests in acid rain formation and high-elevation deforestation, many comprehensive international and national field campaigns on clouds were conducted since the 1980s in North America and Europe (Anderson et al., 1999; Herrmann et al., 2005b; Schemenauer et al., 1995; Wobrock et al., 2001). The majority of these studies focused on continental clouds sampled from high-elevation sites (Bridges et al., 2002; Herckes et al., 2007; Rattigan et al., 2001; Wrzesinsky and Klemm, 2000; Van Pinxteren et al., 2005). A few experiments were carried out in marine environments and by aircraft (Benedict et al., 2012; Straub et al., 2007; Wang et al., 2009). Some observational studies were carried out in East Asia (Japan, Korea, China and India) after the 1990s (Aikawa et al., 2006; Kim et al., 2006; Wang et al., 2011a; Watanabe et al., 2001). In China, investigations of cloud water chemistry started in the 1980s, and limited information on cloud water composition was obtained at a few mountainous sites in southern China (Wang and Xu, 2009). Due to a shortage of equipment and research funding, only pH and a few soluble ions were analyzed in those campaigns. In the following three decades, studies on Chinese cloud chemistry were rare, although the anthropogenic emissions in China have increased dramatically and acid rain became a serious environmental issue in China. Earlier studies indicate that severe acid precipitation was only present in southern and southwestern China, but recent observations have revealed the emergence of acid precipitations in northern China (Tang et al., 2010; Wang et al., 2008).

The North China Plain is in the northern part of the large flatland in eastern China, which is the most populated region of the country and home to intense industrial and agricultural activities. For instance, Shandong Province has the highest SO_2 (3102 Gg/year in 2006) and NO_x (1759 Gg/year in 2006) emissions on a provincial basis in China (Zhang et al., 2009). Mount Tai (Mt. Tai) is the highest mountain in the North China Plain. In recent years, a number of studies have been carried out at the summit of Mt. Tai to investigate photochemical ozone (e.g., Gao et al., 2005), particulate matter (Wang et al., 2011b, 2012; Zhou et al., 2009), and precipitation chemistry (Li et al., 2011b; Wang et al., 2008). As part of China's National Basic Research Program on acid rain, five intensive clouds campaigns were conducted at the summit of Mt. Tai during 2007–2008. To our knowledge, this is the first comprehensive characterization study of cloud composition in northern China. A sub-set of the data (about one month in March–April 2007) has been analyzed focusing on the influence of anthropogenic emissions and sandstorms on ionic composition of cloud and the scavenging of aerosols by cloud in the spring season (Wang et al., 2011a); PAH concentrations in cloud water collected during 2008 winter campaign were examined by Li et al. (2010), and a detailed examination of various aqueous sulfur oxidation pathways in these clouds is given by Shen et al. (submitted for publication). The present study combines all these five campaigns during 2007–2008, and further analyzes the cloud chemical composition (inorganic ions and several organic acids) and its temporal variation, examines the transport of atmospheric pollutants affecting the studied clouds, characterizes the droplet-size dependence of cloud water composition, and investigates the contribution of aqueous chemistry to observed sulfate concentrations by using a tracer method.

2. Experimental

2.1. Measurement sites and instruments

Cloud water samples were collected at the summit of Mt. Tai (36°18N, 117°13E, 1545 m a.s.l), which is located in the North China Plain approximately 230 km from the Bohai Sea and Yellow Sea as illustrated in Fig. 1. A total of 482 cloud water samples (243 bulk samples and 239 drop size resolved samples) were collected in 38 cloud events during five campaigns in 2007 and 2008. Observations in 2007 and 2008 winter were conducted at site 1, and observations in spring and summer of 2008 were performed at site 2 (Fig. 1). Detailed information about the observation periods and collected samples is summarized in Table 1.

During the two campaigns in 2007 and winter of 2008, cloud samples were collected using a Caltech Active Strand Cloud Collector (CASCC) (Demoz et al., 1996). The CASCC is a single stage collector operating at a flow rate of 24.5 m^3 min^{-1} with a lower droplet size cut of 3.5 μm (droplet diameter collected with 50% efficiency). In 2008, a size-fractionating Caltech Active Strand Cloud Collector (sf-CASCC) was added. The sf-CASCC is similar to the CASCC, but contains two collection stages and can collect drop size-resolved samples of cloud water. The sf-CASCC operates at a flow rate of 19 m^3 min^{-1} (Demoz et al., 1996). Large drops are inertially collected from the air stream in the first stage (theoretical 50% size cut of approximately 17 μm) and smaller drops pass through to be collected on the second stage Teflon strands (theoretical 50% size cut of 4 μm).

The collectors were cleaned by high-purity deionized water (>18 MΩ) before sampling, and field blanks were collected periodically and processed by the same analytical procedures as the cloud water samples. Cloud samples were usually collected on an hourly basis. Different cloud events were differentiated from each other by non-cloudy intervals of at least 6 h.

2.2. Sample processing and analysis

Each collected sample was weighed in a field lab. The pH of each unfiltered cloud water sample was measured by a portable pH meter and combination electrode calibrated with pH 4 and 7 buffers. In the 2007 and 2008 winter campaigns, a volume of 200 ml of each original sample was filtered through a cellulose acetate filter (0.45 μm pore size) to remove suspended particulate matter. Samples collected in spring and summer of 2008 were not filtered.

Sample preservation and analysis procedures utilized in this study were previously described by Collett et al. (1999) and are only
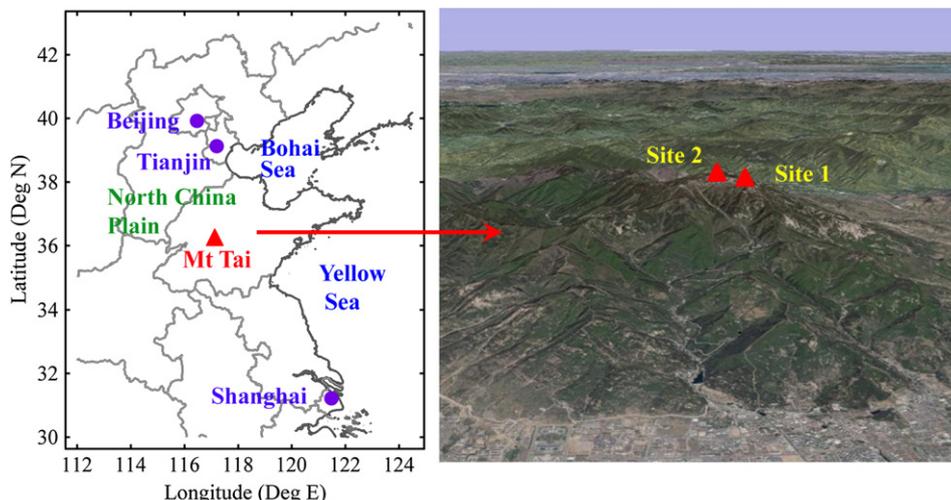
Fig. 1. Map showing the location of Mt. Tai in the North China Plain and the observation sites at the summit of Mt. Tai during 2007–2008.

briefly summarized here. Aliquots for organic acids analysis were preserved by addition of a small volume of chloroform to act as a biocide. Aliquots for trace metal analysis were prepared by acidification with 1% (v/v) trace metal grade nitric acid. HCHO aliquots were prepared by adding a buffered preservation solution containing sulfite to form a stable compound, hydroxymethanesulfonate (HMS). HMS was later decomposed in the laboratory to release HCHO which was analyzed by a fluorescence technique. This method determines the sum of free formaldehyde and HMS present in the solution before preservation. Aliquots for aqueous H_2O_2 analysis were prepared by adding buffered solution containing p-hydroxyphenylacetic acid, and then were analyzed by fluorescence method. For S(IV) aliquots, S(IV) was stabilized as HMS by adding buffered HCHO solution as well as catalase solution to destroy any hydrogen peroxide in the sample. This method provides a measure of total S(IV) comprising free S(IV) and HMS. The preserved S(IV) was analyzed on a UV–Visible spectrophotometer by the para-rosaniline method.

In 2007 and winter of 2008, water soluble inorganic ions (including NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, NO_2^-, NO_3^- and SO_4^{2-}) and organic acids (including formate, acetate and oxalate) were analyzed by ion-chromatography (Dionex, Model 2500). The system employed an IonPac CS12A separator column with methanesulfonic acid eluent for analysis of cations, and an IonPac AS11-HC separator column with NaOH gradient elution for determining inorganic anions and organic acids. The IC system was calibrated using a series of lab-prepared ion standards every day. Calibration accuracy was monitored by injecting independent environmental

reference solutions. The results of cation and anion balances of cloud water are depicted in Fig. 2. As shown, most of the samples present good ion balances, indicating the good quality of the species measurement. Trace elements (such as Fe, Mn and Se) in filtered cloud water in 2007 and 2008 winter were analyzed using Agilent 7500a ICP-MS. The water soluble Se concentrations in aerosols were also analyzed by Agilent 7500a ICP-MS after being extracted in deionized water (>18 MΩ) and pretreated with trace metal grade nitric acid. For cloud samples in spring and summer 2008, the analysis methods for water soluble ions, organic acids and trace elements was described in Shen et al. (submitted for publication).

A Gerber Scientific Particulate Volume Monitor (PVM-100) was used to measure cloud Liquid Water Content (LWC) in 2008. The PVM was not available in 2007, so the LWC for 2007 sampling periods was estimated from the cloud water collection rate. LWC is determined as the collected cloud water amount divided by the air volume passing through the collector during the sampling period

Table 1
Summary of observation periods and samplers used for collecting cloud water at Mt. Tai.

	Location	Campaigns	Collected samples	Collectors
Site 1	Southeast of the summit	15 March–21 April, 2007	38[a]	CASCC
		15 June–18 July, 2007	66[a]	CASCC
		15 October–29 November, 2008	16[a]	CASCC
Site 2	Northwest of the summit	25 March–25 April, 2008	18[a]/50[b]	CASCC, sf-CASCC
		10 June–15 July, 2008	105[a]/189[b]	CASCC, sf-CASCC

[a] Bulk samples.
[b] Drop size resolved samples.
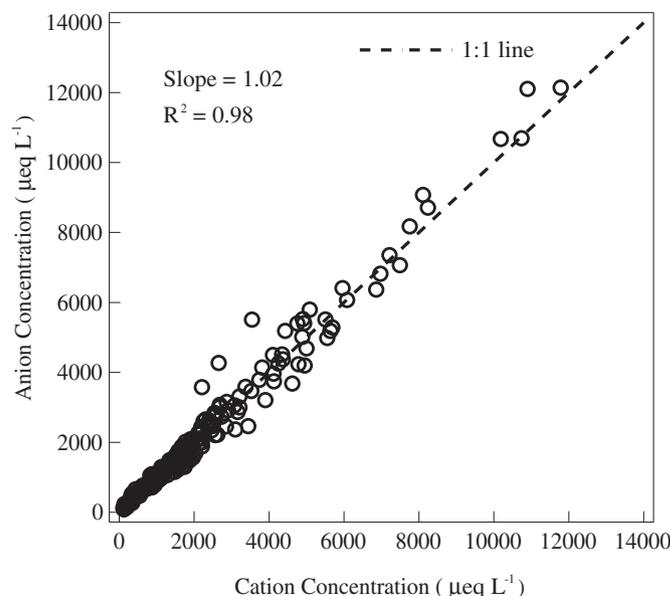
Fig. 2. Data quality plot showing anion and cation balances for all cloud samples at Mt. Tai during 2007–2008.

and the collector efficiency using Eq. (1) (Waldman et al., 1985). The constant 0.8 in the denominator is the estimated collection efficiency for the CASCC (Demoz et al., 1996). Eq. (1) assumes that most of the cloud liquid water content is comprised of drop sizes substantially larger than the 3.5 μm cut size so that the droplet collection efficiency on an individual strand approaches 100% and the overall cloud water collection efficiency is determined mainly by the fraction of air effectively sampled by the CASCC. This is a reasonable assumption for the cloud types studied.

$$LWC = \frac{\text{sample weight(g)}}{\text{sampling interval(min)} \times \text{air volume rate} \left(m^3 min^{-1}\right) \times 0.8}$$

(1)

3. Results and discussion

3.1. Chemical composition of cloud water at Mt. Tai

A statistical summary of different components in cloud of Mt. Tai during 2007–2008 is presented in Table 2. The cloud water pH measured during the five campaigns ranged from 2.56 to 7.64. 80% of the cloud samples had pH values lower than 5.6, and 55% of sample pH values were lower than 4.5, showing a high level of acidification of cloud water in the North China Plain. The volume weighted mean (VWM) pH of cloud water at Mt. Tai over the 2007 and 2008 campaigns was 3.86, which is lower than rain water (pH = 4.7 in 2004–2006 and pH = 4.5 in 2005–2008) at the same site (Li et al., 2011b; Wang et al., 2008). The VWM pH value at Mt. Tai is comparable to the results in North America during the 1980s and 1990s, but is lower than most recent cloud observation results, as shown in Table 3. It should be noted that the calculation methods for mean pH values between studies are different, and the one derived from the mean H^+ concentration would be generally lower than the arithmetic average value of the same dataset. Because of the emission control on acid rain precursors in North America and Europe in the past two decades, cloud/precipitation acidification has been improved in these regions, while the growth in emissions in China has yielded acidic conditions as observed at Mt. Tai.

The ionic composition of cloud water at Mt. Tai was dominated by NH_4^+, SO_4^{2-}, NO_3^- and Ca^{2+}, similar to the precipitation composition at Mt. Tai (Li et al., 2011b; Wang et al., 2008). SO_4^{2-} was the most abundant anion in the cloud water, with an average of 1064 μeq L^{-1} (Table 2). Assuming the equivalent ratio of SO_4^{2-}/Na^+ in seawater salts of 0.12 (Möller, 1990), we determined that the non sea-salt sulfate (nss-SO_4^{2-}) contributed 99.6 ± 0.7% of the total SO_4^{2-} in cloud water of Mt. Tai. The high anthropogenic sulfate contribution in cloud water is consistent with high SO_2 emissions in this region. NO_3^- was the second most abundant anion. The equivalent ratio of VWM nss-SO_4^{2-} to NO_3^- in cloud water was 2.61, which is a little lower than the S/N ratios in rain water at the same site (3.11 in 2007 and 2.84 in 2008) (Li et al., 2011b), and is comparable to the results in cloud water (2.47) observed at Mt. Heng in South China (Sun et al., 2010). The S/N ratios in cloud water at both Mt. Tai and Mt. Heng are larger than most of the values from other mountain sites in Table 3, indicating that SO_2, mainly emitted from coal combustion in power plants, still dominates the acidification of cloud water in many regions of China.

NH_4^+ was the most prevalent cation in cloud water at Mt. Tai, accounting for 36.6% of the total ions. Ca^{2+} also played an important role in acid neutralization in clouds at this continental site. Hutchings et al. (2009) also showed that soil components (Ca^{2+} and Mg^{2+}) largely contributed to neutralizing the acids in cloud water at Mt. Elden and resulted in high pH values of cloud water. A strong sand-storm happened on April 21 in 2007 (Wang et al., 2011a), and the contribution of Ca^{2+} to total ions in cloud water increased from its average level (6%) to 23%. A high Ca^{2+} concentration seems to be an important feature of clouds at Mt. Tai and some other Asia sites, and the Ca^{2+} concentrations were usually several times higher than those in most North American and European sites (Table 3). For Na^+ and Cl^-, the concentrations at Mt. Tai were much lower than those of many other sites, especially sites near seaside, indicating a minor influence of sea salt aerosols at Mt. Tai. Much higher Cl^-/Na^+ ratios (average: 3.72) than seawater (1.17) were observed in Mt. Tai samples, suggesting excess Cl^- in cloud samples which is possibly from emission of anthropogenic HCl produced by waste incineration or power plants using lignite (Wang et al., 2011a).

The VWM concentrations of formic, acetic and oxalic acids were 26.7, 19.4 and 10.4 μeq L^{-1}, respectively, accounting for 3.5% of the total anions. The organic acids contributed to 1.5% of the total free acidity (TFA, determined by calculating the equivalent concentration of dissolved anions and ionized organic acids at the measured cloud pH). It is lower than the contribution of organic acids to TFA (4%) in clouds at Mt. Heng in south China (Sun et al., 2010), and is much lower than that in summer clouds (22%) at Whiteface mountain (Khwaja et al., 1995), suggesting that anthropogenic sources (i.e., SO_2 and NO_x) were still the predominant cause of cloud acidification over the North China Plain.

3.2. Seasonal variation and backward trajectories analysis

The VWM pH of cloud water did not show too much difference between seasons (3.78 in spring, 3.89 in summer, 3.81 in winter), indicating year round acidification of cloud waters in this region. The VWM concentrations of species in cloud water for each campaign are presented in Fig. 3. Both NH_4^+ and SO_4^{2-} showed higher VWM fractions of total ions in summer clouds than in cold seasons (spring and winter) (Fig. 3). Although SO_2 emission increased in winter due to more coal combustion for heating, the observed SO_4^{2-} concentration in clouds at Mt. Tai was lower, which could be possibly explained by the higher LWC in winter than summer (average: 0.25 vs. 0.17 g m^{-3}) and that some of the observed cloud events in the 2008 winter campaign did not cover the heating period in North China. More abundant atmospheric

Table 2
Summary of the concentrations of chemical species in cloud water sampled at Mt. Tai during 2007–2008.

Species	Unit	No. of samples	Range	Median	Mean	VWM[a]
pH	–	243	2.56–7.64	4.34	4.60[b]	3.86
Na^+	μeq L^{-1}	243	0.4–852	17.0	36.3	25.0
NH_4^+	μeq L^{-1}	243	75.8–9111	1133	1515	1215
K^+	μeq L^{-1}	243	1.2–855	32.5	74.6	55.1
Mg^{2+}	μeq L^{-1}	238	BDL[c] –1107	20.2	45.1	33.0
Ca^{2+}	μeq L^{-1}	240	1.6–9054	109	277	193
F^-	μeq L^{-1}	120	1.9–506	19.3	39.5	31.2
Cl^-	μeq L^{-1}	243	3.7–1230	47.1	114.0	93.4
NO_2^-	μeq L^{-1}	223	BDL–155	2.8	6.5	4.3
NO_3^-	μeq L^{-1}	243	21.0–7774	301	600	407
SO_4^{2-}	μeq L^{-1}	243	56.2–9734	976	1373	1064
Formate	μeq L^{-1}	120	BDL–278	3.6	31.8	26.7
Acetate	μeq L^{-1}	120	BDL–113	9.9	23.1	19.4
Oxalate	μeq L^{-1}	120	BDL–119	6.1	11.1	10.4
Se[d]	μg L^{-1}	117	BDL–99.9	9.5	13.2	11.3
Fe[d]	μg L^{-1}	117	BDL–1369	52.3	146	104
Mn[d]	μg L^{-1}	117	BDL–1645	26.8	66.3	45.3
HCHO	μmol L^{-1}	232	BDL–119	10.9	16.6	17.1
H_2O_2[d]	μmol L^{-1}	114	BDL–101	4.7	10.3	10.9
S(IV)	μmol L^{-1}	223	BDL–275	18.4	31.0	27.8

[a] VWM: Volume Weighted Mean Concentration.
[b] Arithmetic average value of all samples pHs.
[c] Below detection limit.
[d] Filtered cloud water samples in 2007 and winter of 2008.

Table 3
Comparison of the concentrations of major ions at Mt. Tai with other mountain sites in the world.

Site	Altitude (m)	Period (year)	pH	Na$^+$ (µeq L^{-1})	NH$_4^+$ (µeq L^{-1})	K$^+$ (µeq L^{-1})	Mg^{2+} (µeq L^{-1})	Ca^{2+} (µeq L^{-1})	Cl$^-$ (µeq L^{-1})	NO$_3^-$ (µeq L^{-1})	SO$_4^{2-}$ (µeq L^{-1})	S/N	Reference
Mt. Moosilauke, USA	962	1986–1988	3.36[a]	18[d]	179	4	7	14	24	231	448	1.94	Li and Aneja (1992)
Mt. Mitchell, USA	1950	1986–1988	3.34[a]	19[d]	218	8	14	55	33	205	576	2.81	Li and Aneja (1992)
Mount Tremblant, Canada	860	1985–1991	3.74[a]	10[d]	239	5	23	70	13	170	339	1.99	Schemenauer et al. (1995)
Whiteface Mountain, USA	1483	1994	3.7[b]	2[e]	149	2	5	15	8	99	282	2.85	Aleksic et al. (2009)
Whiteface Mountain, USA	1483	1997	3.74[b]	6[e]	167	2	10	34	10	134	273	2.04	Anderson et al. (1999)
Whitetop Mountain, USA	1686	1997	3.63[b]	14[e]	211	3	8	21	26	156	329	2.11	Anderson et al. (1999)
Clingman's Dome, USA	2014	1997	3.50[b]	16[e]	239	3	11	41	24	180	424	2.36	Anderson et al. (1999)
Waldstein, Germany	800	Apr–Oct 1997	4.3[c]	65[d]	669	12	20	69	54	481	497	1.03	Wrzesinsky and Klemm (2000)
Zinnwald, Germany	877	1997–1998	4.00[b]	52[e]	560	23	12	56	48	176	561	3.19	Zimmermann and Zimmermann (2002)
Vosges Mountain, France	1146	1998–1999	4.82[c]	175[d]	276	57	26	120	143	181	298	1.65	Herckes et al. (2002)
Mt. Rokko, Japan	931	Jun–Nov 1999	3.71[b]	553[e]	346	24	144	202	441	456	390	0.86	Aikawa et al. (2006)
Mt. Awaga, Japan	962		4.10[b]	152[e]	171	10	36	36	155	123	196	1.59	Aikawa et al. (2006)
Puy de Dôme, France	1465	2001–2002	5.29[c]	29[d]	147	5	12	15	59	103	85	0.83	Marinoni et al. (2004)
Daekwanreuang, Korea	840	2003	4.4[a]	166[d]	611	28	68	198	166	494	489	0.99	Kim et al. (2006)
Stóg Izerski, Poland	1060	2003–2004	4.44[a]	101[d]	190	21	27	65	97	177	137	0.77	Blas et al. (2008)
Szrenica, Poland	1332	2003–2004	4.25[a]	67[d]	167	6	21	52	66	173	133	0.77	Blas et al. (2008)
Whiteface Mountain, USA	1483	2006	3.88[b]	4[e]	149	2	7	27	7	79	220	2.78	Aleksic et al. (2009)
Mt. Elden, USA	2834	2005–2007	5.12–6.66	40–630	20–680	BDL[f]–60	BDL[f]–490	30–1090	20–730	130–1670	60–570	0.29–0.69	Hutchings et al. (2009)
Mt. Heng China	1279	2009	3.80[b]	66[e]	356	17	11	60	21	159	392	2.47	Sun et al. (2010)
Mt. Tai, China	1545	2007–2008	3.86[b]	25[e]	1215	55	33	193	93	407	1064	2.61	The present work

[a] Mean pH values calculated from average H$^+$ concentration.
[b] VWM (volume weighted mean) pH values calculated from the VWM H$^+$ concentration.
[c] Mean pH: Arithmetic mean of pH values.
[d] Average ions concentrations.
[e] Volume Weighted Mean concentrations of ions.
[f] Below detection limit.

oxidants in summer that can increase the production efficiency of sulfate also contribute to the higher SO_4^{2-} fraction in summer clouds. The enrichment of NH_4^+ in summer is consistent with increased agriculture activity in summer and more efficient ammonia emissions at higher temperature. Higher fractions of soil/crustal ions Ca^{2+} and Mg^{2+} were observed in spring and winter (Fig. 3), when dry continental air masses were more frequent under the condition of winter monsoon in cold seasons. The air parcel could bring more soil dust from deserts and from the bare lands with little vegetation in North China, and consequently enhance the cloud's soil/crustal ion levels.

To identify the origins and transport pattern of the sampled air masses, 3-dimensional 72-h backward trajectories terminating at the peak of Mt. Tai (1500 m a.s.l.) were derived by using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT Model – http://ready.arl.noaa. gov/HYSPLIT.php) with GDAS meteorological data (global, 2006 to present – ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1/). Cloud samples were subsequently classified into four air transport history groups as Northwest (NW), Southwest (SW), Southeast (SE) and Northeast (NE). The typical trajectories of the four groups, as well as a pie chart depicting cloud water ionic fractions associated with each group, are plotted in Fig. 4.

Among the four identified groups, most of the air masses (87%) originated from the southern parts of China (i.e., SW and SE). The cloud water in these air masses had lower pH values than that from the north, and this confirms the previous result of using only 2007 spring data (Wang et al., 2011a). Southern China has suffered from acidic precipitations for a long time as a result of the extensive use of high sulfur coal and the lack of neutralizing species in local soils (e.g., Wang and Wang, 1996).

The air masses in the SE group, which passed through the east part of Jiangsu and the southern part of Shandong provinces, were characterized by the highest NO_3^- fraction and the lowest pH value (VWM pH of 3.80). The correlation between NO_3^- and H^+ suggests an important contribution of NO_x emissions to acidic cloud water because of the enhanced NO_x emission in the coastal regions, especially in the fast developing Yangtze Delta region. Li et al. (2011a) reported a lower S/N ratio (1.16) in fog waters in urban
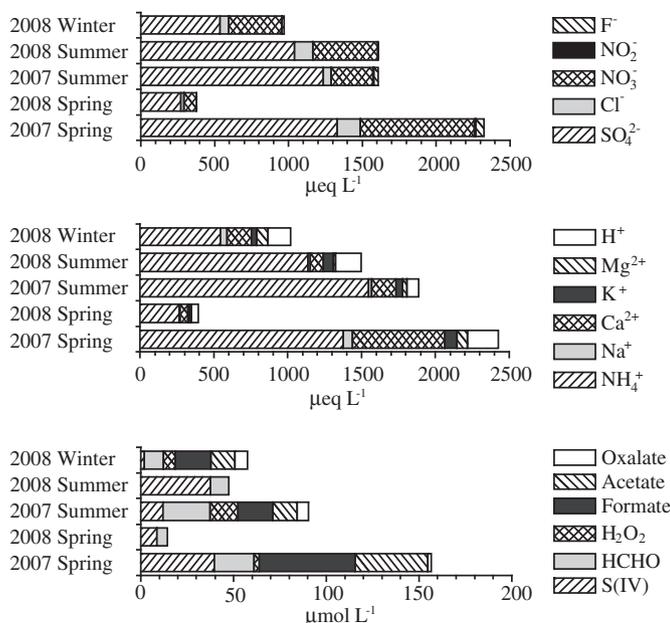
Fig. 3. The volume weighted mean (VWM) ionic concentrations in cloud water collected at Mt. Tai in five intensive campaigns during 2007–2008.

Shanghai than that in cloud waters at Mt. Tai. A decreasing trend of S/N ratio in rain water at Mt. Tai (3.98−2.84 during 2005−2008) has been reported by Li et al. (2011b), suggesting increasing NO_x emissions in the North China Plain. While the SO_4^{2-} concentration is still higher than NO_3^- in precipitation, national acid rain monitoring data show that the center of acid rain in the south has expanded eastwards as a result of high NO_x emissions in the coastal regions (Tang et al., 2010). Therefore more attention should be paid to the increasing influence of NO_x emissions on cloud and precipitation acidification.

Higher concentration of soil/crustal components (Ca^{2+} and Mg^{2+}) and the highest average pH value were found in air masses in the NW category (Table S1), which originated from arid or semi-arid region in northwest China. When air masses pass through the saline and alkaline lands in northwestern China, erosion and subsequently transported soil/dust aerosols play an important role in moderating H^+ fractions in clouds formed later. In addition, Na^+ was also more enriched in NW category compared to other groups, whereas the Cl^- concentration did not show much difference between categories, thus resulting in the lowest Cl^-/Na^+ ratio (1.56) in NW category (Table S1). The enrichment of Na^+ in NW direction was possibly associated with the contribution of halite (NaCl) in dust aerosols in China's northwest. Okada and Kai (2004) have found that halite originated from salt flats accounted for 10% of dust particles collected in the Taklimakan desert. Shen et al. (2009) also observed a larger Na^+ fraction in aerosols during dust period than normal days, and a lower Cl^-/Na^+ ratio (0.51) in air masses from northwest China than the normal level (2.27).

3.3. Droplet-size dependence of cloud water composition

The relation of chemical composition to cloud droplet size appears to depend on the type of clouds as well as the chemical mix of gases and aerosols. Some studies have found concentrations of NH_4^+, SO_4^{2-}, NO_3^- and H^+ enriched in smaller drops and crustal species enriched in larger drops (Hoag et al., 1999; Ogren et al., 1992; Reilly et al., 2001). Some orographic clouds, however, were observed to contain higher solutes concentrations in larger cloud drops (Noone et al., 1988; Schell et al., 1997). Observations of intercepted clouds at Whiteface Mountain revealed a size independence of the major ions SO_4^{2-}, NH_4^+ and NO_3^- (Moore et al., 2004).

We compared the concentrations of major ions in the large and small size bins collected by the two-stage sampler in summer 2008 at Mt Tai. As shown in Fig. 5, the ion's size dependence varied with different species. Small drops were more acidic than large drops. For crustal ions, Ca^{2+}, Mg^{2+} and Na^+ showed elevated concentrations in large drops. The anthropogenic ions, NH_4^+ and SO_4^{2-}, appeared to be independent of drop size, i.e. evenly distributed between large and small drops. NO_3^- tended to be slightly enriched in larger droplets.
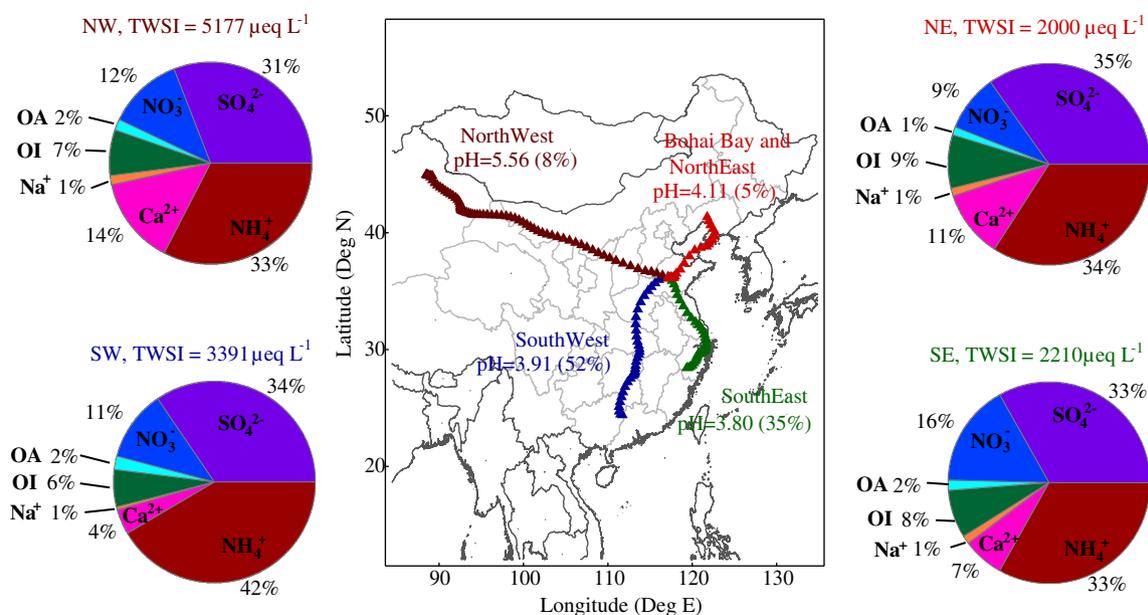
Fig. 4. Representative backward trajectories arriving at Mt Tai for 4 air-mass categories and the contribution of different species to total water soluble ions in each air-mass category. The summary of species concentrations in each category is provided in a supplementary table (Table S1). TWSI: Total Water Soluble Ions; OI: Other Ions; OA: Organic Acids.
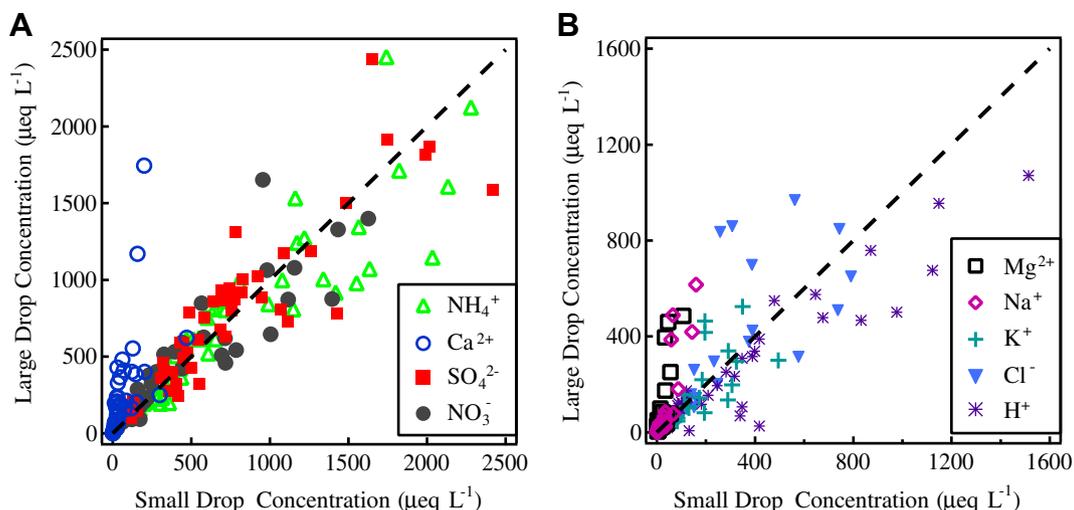
Fig. 5. Scatter plot of the concentrations of ions in the large and small drop size fractions collected using the sf-CASCC.

A further examination of the ratios of concentrations in large and small drops revealed a dependence of their relative concentrations as a function of cloud evolution time, as shown in Fig. 6. In the initial stage of the cloud events, the major ions (SO_4^{2-}, NH_4^+ and NO_3^-) were observed more enriched in large drops, and their enrichment tended to increase during the first 3 h, and then started to decrease; after 6 h on average, these ions started to enrich in small drops. Ca^{2+} was consistently enriched in large drops;
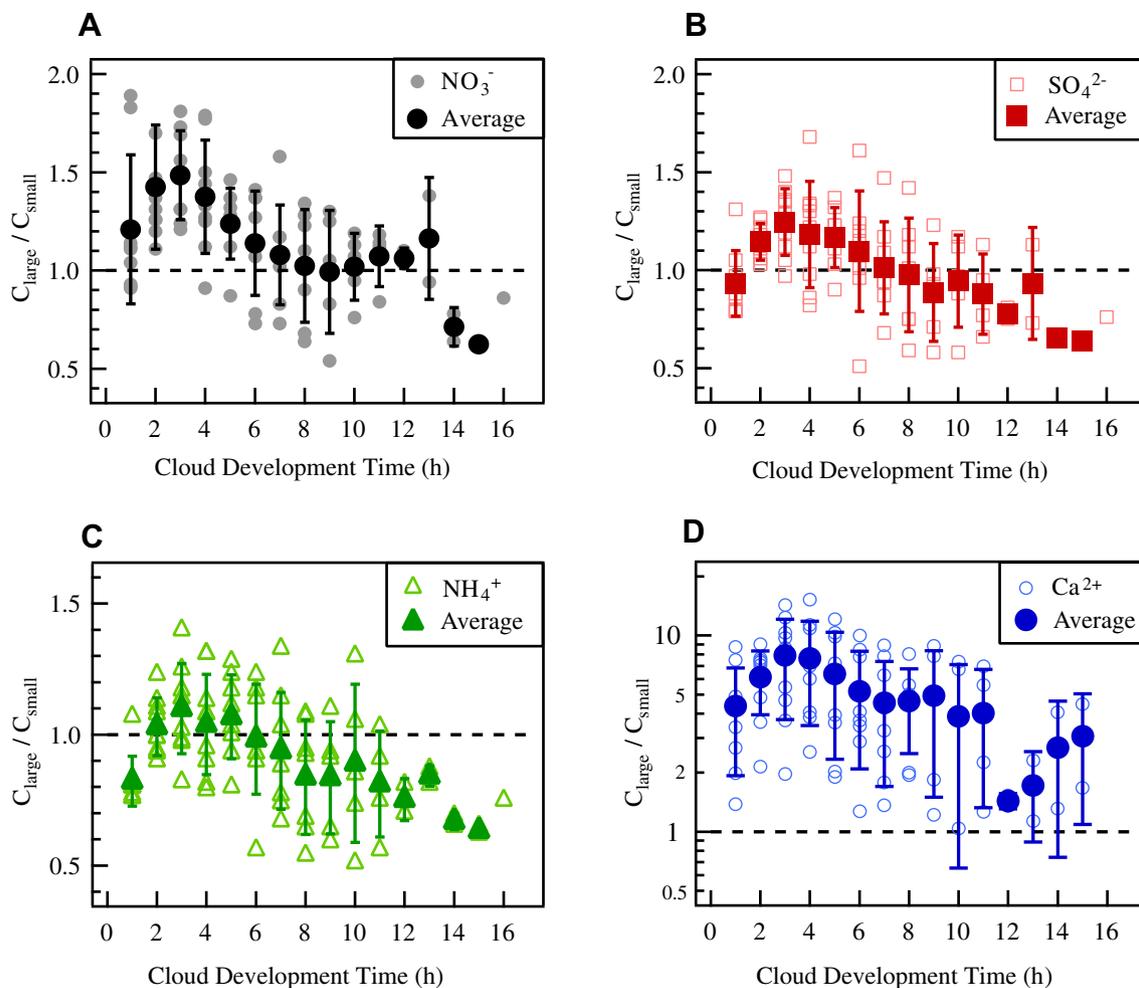
Fig. 6. The ratios of ionic concentrations in large and small drops (C_{large}/C_{small}) for (A) NO_3^-, (B) SO_4^{2-}, (C) NH_4^+ and (D) Ca^{2+} as a function of time during cloud events. The gray and open markers are the data for each cloud event, and the solid markers represent the average value for each hour along the cloud evolution, and the error bars show the standard deviations.
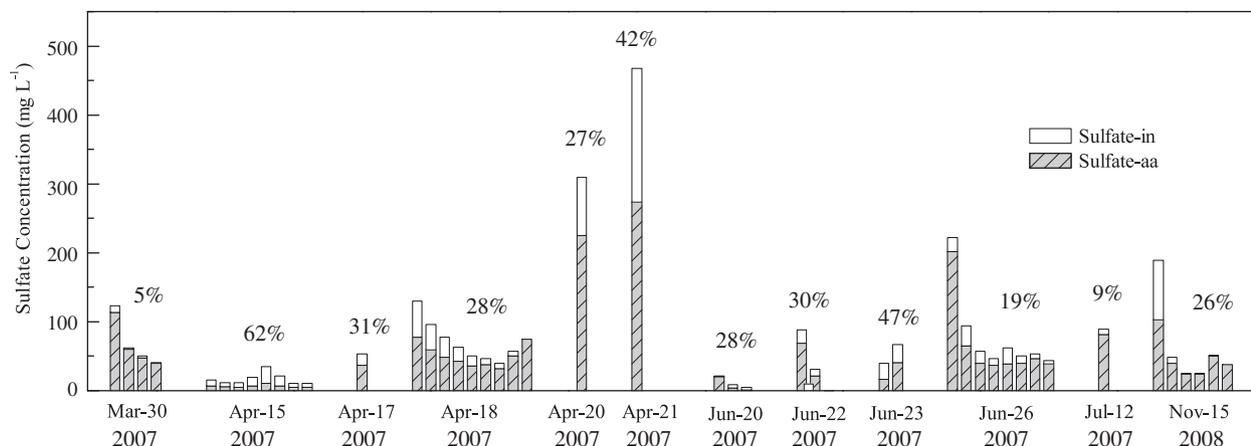
Fig. 7. In-cloud produced sulfate (Sulfate-in) and scavenged sulfate (Sulfate-aa) determined by Se-tracer method for cloud samples collected at Mt. Tai during spring and summer of 2007 and winter of 2008.

nonetheless, there was still a decreasing enrichment trend as a function of cloud duration. The temporal variation of size-dependency during cloud events is related to the change of CCN size distribution during cloud evolution and other factors/processes (Schell et al., 1997). For instance, in the early stage of cloud, activation of large particles can result in higher solute concentrations in large droplets, and in the later period of cloud, the droplets can only be formed by activation of smaller particles. In addition, the uptake of gas pollutants and the following aqueous phase reactions and deposition could also be affected by the droplet size, contributing to the change of solute concentrations in different size of droplets. Considering so many factors can influence the drop size-dependence of cloud solute concentrations and its temporal evolution, the observations here are not sufficient to permit us to draw any conclusions about responsible mechanisms.

3.4. Estimate of aqueous production of sulfate by Se-tracer method

The SO_4^{2-} in cloud water comes both from scavenged aerosol particles and from in-cloud aqueous sulfate production by the oxidation of SO_2 absorbed from the gas phase. Previous studies have demonstrated that the aqueous oxidation of SO_2 is much more rapid than gas-phase oxidation and that, globally, more than 80% of sulfate in atmospheric particles was formed through in-cloud aqueous oxidation (Langner and Rodhe, 1991). Aqueous sulfate formation is also of interest since sulfuric acid produced by in-cloud SO_2 oxidation will directly result in the acidification of cloud droplets. Considering the high atmospheric SO_2 level in the study region and frequent clouds at the site, the aqueous formation of sulfate could make a significant contribution to the sulfate aerosol loading and cloud acidification in this region.

The amount of sulfate produced in cloud droplets can be calculated from the numerical simulation of aqueous oxidation rates of S(IV) by H_2O_2, O_3, O_2 (catalyzed by Fe and Mn) and radical oxidants. Shen et al. (submitted for publication) look at the relative importance of these aqueous sulfur oxidation pathways using field observations of key cloud and gas phase constituents (e.g., pH, oxidant concentrations, catalyst concentrations). However, it is challenging to directly confirm such calculations from field observations because the SO_4^{2-} derived from aerosol scavenging and in-cloud aqueous oxidation is chemically indistinguishable (Burkhard et al., 1995). Husain (1989) proposed a method for direct determination of in-cloud produced sulfate using a selenium (Se) tracer technique. Selenium and sulfate tend to co-occur in air

masses because coal combustion is a dominant source of each. The essence of this tracer method is that the only source of Se in cloud droplets is scavenging of aerosols and, thus, Se can be used as a tracer for sulfate scavenged from aerosols. The in-cloud produced sulfate $(SO_4^{2-})_{in}$ can then be determined by Eq. (2)

$$(SO_4^{2-})_{in} = \left[\left(\frac{SO_4^{2-}}{Se} \right)_{cw} - \frac{\alpha}{\beta} \times \left(\frac{SO_4^{2-}}{Se} \right)_{aa} \right] \times (Se)_{cw} \qquad (2)$$

in which the subscripts cw and aa stand for cloud water and ambient aerosol, respectively; α and β are the scavenging coefficients of SO_4^{2-} and Se, and a value of 1.0 for α/β was adopted following Burkhard et al. (1995) and Husain et al. (2004).

The in-cloud sulfate production in cloud events at Mt. Tai are presented in Fig. 7, in which the SO_4^{2-} contributed by ambient aerosol $(SO_4^{2-})_{aa}$ and in-situ formation $(SO_4^{2-})_{in}$ are depicted as solid and blank bars, respectively. As shown, the average percentage of in-cloud production of sulfate to total sulfate is 27%, ranging from 5% to 62% for individual cloud event. The result is comparable to that obtained at Whiteface Mountain in 1990–1998 (mean value = 24%, range: below detection to 62%) by Rattigan et al. (2001).

It should be noted that the average fraction of 27% here was derived from one single cloud processing event. It does not contradict the previous claim that more than 80% of SO_4^{2-} in the aerosol phase is formed from aqueous phase SO_2 oxidation. Each aerosol particle that acts as a CCN may go through 3−7 cloud cycles before being removed from the atmosphere. Thus, aerosol sulfate can be accumulated through several cloud processing events. Considering the frequent aerosol−cloud cycles and the abundant oxidants at Mt. Tai in summer (see more detailed discussion in Shen et al. (submitted for publication)), a higher efficiency of sulfate production should be expected in summer. Indeed, the ratio of SO_4^{2-} to Se in pre-cloud aerosols in summer is 1.6 times of the average value in winter and spring aerosols.

4. Summary and conclusions

Intensive observations of cloud chemistry were conducted at the summit of Mt. Tai in the North China Plain during 2007−2008. Cloud water samples were collected by single and two-stage could samplers (CASCC and sf-CASCC), and the chemical composition of collected cloud water was analyzed. The volume weighted mean pH of all clouds samples at Mt. Tai was 3.86, and more than half of the

samples were strongly acidified (pH < 4.5), indicating the high acidification level of cloud water in the North China Plain. The dominant ion species were NH_4^+, SO_4^{2-}, NO_3^- and Ca^{2+}, while organic acids only had a minor contribution (1.5%) to the total free acidity in cloud water. The fractions of NH_4^+ and SO_4^{2-} in total ions were higher in summer clouds, while Ca^{2+} was enriched in cold seasons. The backward trajectory analysis showed that most of the air masses (87%) originated from the southern parts of China, and cloud water in these air masses was the more acidic. Air masses that originated from North China usually yielded more Ca^{2+} in cloud water and resulted in higher pH values. Concurrent enhancements in NO_3^- and acidity were observed in clouds formed in air masses passing through the fast developing coastal regions of China, suggesting an increasing contribution of NO_x and its atmospheric oxidation products to cloud acidification.

The abundance of ions varied with the size of cloud droplets at Mt. Tai. The smaller droplets were more acidified, and the crustal ions were enriched in larger droplets. The major ions NH_4^+, SO_4^{2-} and NO_3^- exhibited apparent size independence of ions; however, their size distribution actually varied with cloud evolution, with a higher concentration in larger drops in the initial stage and an opposite dependence in the later stage. Application of a Se-tracer method suggests that the sulfate produced through aqueous phase oxidation accounted for 5–62% of the total cloud water sulfate in individual cloud events, with an average of 27%. Higher SO_4^{2-}/Se ratio in summer aerosols indicates a higher efficiency of sulfate production in the season. The results of this study reveal that cloud water at Mt. Tai has been strongly influenced by anthropogenic emissions. This finding also has important implications for the radiative budget and regional climate in eastern China as the anthropogenic impact may also influence cloud physical properties such as droplet size and the lifetime of clouds.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.atmosenv.2012.07.016.

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