https://doi.org/10.5194/acp-2020-1146
Preprint. Discussion started: 27 November 2020

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Inter-annual variations of wet deposition in Beijing during 2014-2017: implications of below-cloud scavenging of inorganic aerosols

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https://doi.org/10.5194/acp-2020-1146
Preprint. Discussion started: 27 November 2020

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Abstract

Wet scavenging is an efficient pathway for the removal of particulate matter (PM) from the atmosphere. High levels of PM have been a major cause of air pollution in Beijing but have decreased sharply under the Air Pollution Prevention and Control Action Plan launched in 2013. In this study, four years of observations of wet deposition have been conducted using a sequential sampling technique to investigate the detailed variation in chemical components through each rainfall event. We find that the major ions, SO_4^{2-}, Ca^{2+}, NO_3^- and NH_4^+, show significant decreases over the 2013-2017 period (decreasing by 39%, 35%, 12% and 25%, respectively), revealing the impacts of the Action Plan. An improved sequential sampling method is developed and implemented to estimate the contribution of below-cloud and in-cloud wet deposition over the four-year period. Overall, below-cloud scavenging accounts for between half and two thirds of wet deposition of the four major ions, with the highest contribution for NH_4^+ at 65% and lowest for SO_4^{2-} at 50%. The contribution of below-cloud scavenging for Ca^{2+}, SO_4^{2-} and NH_4^+ decreases from above 50% in 2014 to below 40% in 2017. This suggests that the Action Plan has mitigated PM pollution in the surface layer and hence decreased scavenging due to the washout process. In contrast, we find little change in the annual volume weighted average concentration for NO_3^- where the contribution from below-cloud scavenging remains at ~44% over the period 2015-2017. While highlighting the importance of different wet scavenging processes, this paper presents a unique new perspective on the effects of the Action Plan and clearly identifies oxidized nitrogen species as a major target for future air pollution controls.

Key words: wet scavenging, below-cloud, in-cloud, deposition, $PM_{2.5}$

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1 Introduction

Atmospheric wet deposition is a key removal pathway for air pollutants and is governed by two main processes: in-cloud and below-cloud scavenging (Goncalves et al., 2002; Andronache, 2003, 2004a; Henzing et al., 2006; Sportisse, 2007; Feng, 2009; Wang et al., 2010; Zhang et al., 2013). The below-cloud scavenging process depends both on the characteristics of the rain, including the raindrop size distribution and rainfall rate, and on the chemical nature of the particles and their concentration in the atmosphere (Chate et al., 2003). Previously, below-cloud scavenging was thought to be less important than in-cloud processes and was simplified or even ignored in many global and regional chemical transport models (CTMs) (Barth et al., 2000;Tang et al., 2005;ENVIRON.Inc, 2005;Textor et al., 2006;Bae et al., 2010). However, more recent extensive research on wet scavenging has found that precipitation, even light rain, can remove 50-80% of the number or mass concentration of below-cloud aerosols, and this is supported by both field measurements and semi-empirical parameterizations of below-cloud scavenging in models (Andronache, 2004b;Zhang et al., 2004;Wang et al., 2014). Xu et al. (2017;2019) studied the below-cloud scavenging mechanism based on the simultaneous measurement of aerosol components in rainfall and in the air in Beijing. They found that below-cloud scavenging coefficients widely used in CTMs were 1-2 orders of magnitude lower than estimates from observations. This implies that the simulated below-cloud scavenging of aerosols might be significantly underestimated. This could be one reason for the underestimation of SO_4^{2-} and NO_3^- wet deposition in regional models of Asia reported in phase II and III of the Model Inter-Comparison Study for Asia (MICS-Asia) (Wang et al., 2008;Ge et al., 2020) and in global model assessments by the Task Force on Hemispheric Transport of Atmospheric Pollutants (TF-HTAP) (Vet et al., 2014). Bae et al. (2012) added a new below-cloud scavenging parameterization scheme in the CMAQ model and improved the simulation of aerosol wet deposition fluxes in East Asia by as much as a factor of two compared with observations. The below-cloud scavenging process is critical not only for wet deposition but also for the concentration of aerosols in the air and it should be represented appropriately in CTM simulations.

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It is important to recognize the contribution of below-cloud scavenging to total wet deposition. However, many studies have found that it is difficult to separate the two wet scavenging processes based on measurement methods alone (Huang et al., 1995;Wang and Wang, 1996;Goncalves et al., 2002;Bertrand et al., 2008;Xu et al., 2017). A commonly used approach to separating below-cloud scavenging from total wet deposition is through sequential sampling (Aikawa et al., 2014;Ge et al., 2016;Aikawa and Hiraki, 2009;Wang et al., 2009;Xu et al., 2017). In this way, precipitation composition during different stages of a rainfall event can be investigated separately in the lab after sampling. The chemical components in later increments of rainfall are thought to be less influenced by the below-cloud scavenging process than by the in-cloud rainout process (Aikawa et al., 2014;2009). Xu et al. (2017) applied this approach to summer rainfall in Beijing in 2014 and found that more than 50% of deposited sulfate, nitrate and ammonium ions were from below-cloud scavenging. In this study, an innovated method based on exponential curve to chemical ions in rainfall by sequential sampling is developed and implemented to estimate the ratio of below-cloud to in-cloud wet deposition in Beijing over the four-year period between 2014 and 2017. Together with $PM_{2.5}$ concentration measurements, the washout effects of the decreasing air pollutants at near-surface due to the Air Pollution Prevention and Control Action Plan (Action Plan) launched in 2013 (State Council of the People's Republic of China, 2019) is also investigated to explore the implications of the Action Plain to the precipitation chemistry.

2 Data and methods

2.1 Measurement site and sampling methodology

The measurement site is located on the roof of a two-floor building at the Institute of Atmospheric Physics tower site (IAP-tower, 39° 58′ 28″ N, 116° 22′ 1″ E) in northern Beijing. It is a typical urban site between the 3rd and 4th ring roads and lying close to the Badaling expressway (Xu et al., 2017;2019;Sun et al., 2015). Four years of Inter-annual observations of each rainfall event were conducted at this site. Sequential sampling of each rainfall event is employed to catch the evolution of precipitation composition during each event. To investigate the detailed variation in the concentration

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of different chemical components in precipitation, especially the sharp changes occurring during the onset of rainfall, high resolution sampling of rainfall at 1 mm sequential increments was performed using an automatic wet-dry sampler. The rainwater collector uses a circular polyethylene board with a 30 cm diameter and collects up to eight fractions. About 70 ml of rainwater is collected for each of the first seven fractions and the rest of the rainfall is collected in the eighth fraction. Rainfall events where eight fractions are collected and identified as full events, and those with fewer than eight fractions are characterized as incomplete events. Manual sampling methods were used to collect more than eight fractions during heavy rainfall, and these are characterized as extended events. Altogether, 69 full events and 6 extended events were recorded over the 2014-2017 period in Beijing.

After collection, all samples are refrigerated at 0-4 ºC and analyzed at the Key Laboratory for Atmospheric Chemistry, Chinese Academy of Meteorological Sciences (CAMS) within one month, following the procedure used for the Acid Rain Monitoring Network run by the China Meteorological Administration (CMA-ARMN) (Tang et al., 2007;2010). Nine ions that include four anions (SO_2^{4-}, NO_3^-, Cl^- and F^-) and five cations (NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) are detected using ion chromatography (IC, Dionex 600, USA). Their relative standard deviations in reproducibility tests are less than 5%. Quality assurance is carried out using routine standard procedure of blind sample inter-comparison organized by CMA (Tang et al., 2010). Quality control is conducted by assessment of the anion-cation balance and by comparison of the calculated and measured conductivity. A more detailed description of the procedure can be found in Ge at al. (2016) and Xu et al. (2017).

2.2 Aerosol measurements

Aerosol mass concentration is recorded in routine measurements for the observation network of the China National Environmental Monitoring Center (CNEMC). $PM_{2.5}$ concentrations are used from the Olympic Park station, a monitoring station located 3 km to the northeast of the IAP-tower sampling site. In addition, an Ambient Ion Monitor-Ion Chromatograph (AIM-IC) developed by URG Corp., Chapel Hill, NC and Dionex Inc., Sunnyvale, CA, is used to measure $PM_{2.5}$ composition at the sampling site

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between 2014 and 2017. This instrument includes a sample collection unit (URG 9000-D) for collection of water-soluble gases and particles in aqueous solution and a sample analysis unit (two ion chromatographs, Dionex ICS-2000 and ICS-5000) for analysis of both anions and cations. The limit of detection of AIM-IC is 0.08 mg/m^3 for NH^{4+} and 0.1 mg/m^3 for the other ions. Aerosol mass concentrations and composition are both measured at 1 h time resolution. Detailed descriptions of the AIM-IC instrumentation can be found in Malaguti et al. (2015) and Markovic et al. (2012). The average concentration of aerosols in the 6 h before each rainfall event is calculated to reflect the air pollution conditions before the event. For comparisons, the yearly average concentration of aerosols has been calculated to represent the normal conditions.

2.3 Estimation of below cloud scavenging

Previous studies have shown that the concentration of chemical ions in precipitation decreases through the progression of a rainfall event and eventually stabilizes at low levels (Aikawa and Hiraki, 2009;2014;Ge et al., 2016;Xu et al., 2017). The rainout and washout contributions to total wet deposition are estimated based on the assumption that the concentrations in later increments can be attributed to scavenging by rainout only. This assumption relies on the efficient scavenging of air pollutants below cloud through the evolution of precipitation. However, the concentration of chemical ions in precipitation may also be affected by many other factors in addition to below-cloud air pollutant concentrations and in-cloud rainout processes. For example, the precipitation intensity may affect the scavenging efficiency of air pollutants below cloud and hence influence wet deposition (Andronache, 2004b;Wang et al., 2014;Xu et al., 2017;2019). Yuan et al. (2014) reported that in central North China high intensity rainfall events of short duration (lasting less than 6 h) are dominant rather than long-duration rainfall that is more common in the Yangtze River Valley. Therefore, the time window for the definition of in cloud stage is very important for estimating the below cloud and in cloud contributions. Previous studies have estimated the concentration of chemical ions scavenged in-cloud based on the subjective judgment that 5 mm of accumulated precipitation is sufficient to identify the contribution of the rainout process (Wang et al., 2009;Aikawa and Hiraki, 2009;Xu et al., 2017). Based on this approach, the

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concentration of NO_3^- and SO_4^{2-} in cloud in Japan was found to be 0.70 and 1.30 mg/L, respectively (Aikawa and Hiraki, 2009). In Beijing, high concentration of NH_4^+, SO_4^{2-} and NO_3^- during 2007 were found at 2.1~5.5, 3.1~14.9, 1.5~5.9 mg/L, respectively (Wang et al., 2009;Xu et al., 2017).

In this study, a new method based on fitting a curve to the chemical ion concentrations with successive rainfall increments has been developed to estimate the contribution of the rainout process. As shown in Figure 1, an exponential curve is fitted to the median, 25th and 75th percentiles of the chemical ion concentrations in each fraction through the rainfall increments. In theory, the concentration of chemical ions stabilize at higher rainfall increments and this represents the concentration in cloud. However, the decrease during each rainfall event is distinctly different, and this regression method is not fully applicable to all rainfall events in practice. Therefore, the exponential regression method is used to estimate the in-cloud concentration under most circumstances, but where the decreasing trend with the increment of rainfall is not significant, the average value of rainfall increments 6-8 of the event is used. The below cloud contributions to wet deposition of each species are then calculated using the following equations (1-2):

$$\mathrm{Wetdep}_{\mathrm{below-cloud}} = \sum_{i=1}^{n}(C_i - \bar{C}) \times P_i \quad (1)$$

$$\mathrm{Contribution}_{\mathrm{below-cloud}} = \frac{\mathrm{Wetdep}_{\mathrm{below-cloud}}}{\sum_{i=1}^{n} C_i \times P_i} \quad (2)$$

Where, C_i, and $\bar{C}$ represent the concentration of each chemical ion in fraction *i* and in cloud and P_i represents the volume of rainfall.

3 Results and Discussion

3.1 Inter-annual variations in chemical components

Significant declines in atmospheric $PM_{2.5}$ concentration have been observed nationwide between 2013 and 2017 during the Action Plan (Zhang et al., 2019). However, few studies have investigated the benefits of the Action Plan for wet deposition. A significant increase in NO_3^- in precipitation of 7.6% was observed at a regional background station in North China between 2003 and 2014 (Pu et al., 2017). An decrease in the ratio of SO_4^{2-}/NO_3^- mostly due to the decreasing of SO_4^{2-} and increasing

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of NO_3^- suggests the transformation of sulfuric acid type to a mixed type of sulfuric and nitric acid in North China. However, the updated record especially after the Action Plan is important to assess the mitigation of the air pollutants not only in the atmosphere but also in rainfall. A nationwide investigation of the wet deposition of inorganic ions in 320 cities across China was recently made based on observations between 2011 and 2016 from the National Acid Deposition Monitoring Network (NADMN), which was established by the China Meteorological Administration (Li et al., 2019). Briefly, both SO_4^{2-} and NO_3^- across China experienced significant changes before and after 2014, with increases from 2011 to 2014 and then decreases from 2014 to 2016. In order to quantify the influence of the Action Plan on wet deposition in Beijing, four years of observations of each rainfall event are considered in this study. Figure 2 shows the volume weighted average (VWA) of inter-annual mean concentrations of SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+} observed in Beijing during 2014 to 2017 along with those reported before 2010 from previous studies (Yang et al., 2012;Pan et al., 2012, 2013) (more detail is provided in Table S1 in supplementary materials). A continuous decrease in VWA concentrations between 1995 and 2017 is found for SO_4^{2-} and Ca^{2+}, with decreases of 46% and 542% in the earlier stage (1995-2010) and decreases of 39% and 35% in the later stage (2014-2017). For NO_3^- and NH_4^+, increases are found during the earlier stage (~60%) and decreases in the later stage (12% for NO_3^- and 25% for NH_4^+). All four components in the later stage show significant decreases, especially for NO_3^- and NH_4^+, suggesting that the Action Plan, which was implemented over this period, has a substantial impact. While Ca^{2+} and SO_4^{2-} played a prominent role in precipitation during the earlier stage before 2010, NH_4^+ and NO_3^- became the primary components in the later stage after 2010. It should be noted that NH_4^+ has a double role in environment pollution because it mitigates acid rain through neutralization, but also acidifies the soil by nitrification. Hence, while sulfur in precipitation has been further reduced under the Action Plan, additional attention is needed for nitrogen to prevent deterioration of the environment by acid rain resulting from nitrate and ammonium.

3.2 Relationship in concentrations in precipitation and the atmosphere

Wet deposition of a substance involves its removal from the associated air mass. The

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scavenging ratio H can be estimated by comparing the monthly average concentration in precipitation with that in the air (Okita et al., 1996;Kasper-Giebl et al., 1999;Hicks, 2005;Yamagata et al., 2009). Xu et al. (Xu et al., 2017) first calculated the rainfall event H based on the hourly concentration of aerosol components measured with an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) and AIM-IC in 2014. In this study four years of observation of aerosol components have been undertaken by AIM-IC. Measurements made in the 6 hours before each rainfall event are averaged to represent the precondition of wet deposition precursors in the atmosphere. Figure 3 shows the relationship between the major chemical ions in precipitation and in the air. The VWA concentration of SO_4^{2-}, NO_3^- and NH_4^+ (hereafter SNA) as well as Ca^{2+} in each rainfall event has been calculated and compared with that in the first 1 mm rainfall fraction, F1#. As shown in Figure 3, positive correlations are found between the concentrations of ions in precipitation and in air, with Pearson correlation coefficients (R) generally higher than 0.7 ($p<0.01$). The concentration in the first fraction should represent a high proportion of below-cloud scavenging due to the washout of air pollutants below clouds by the first rainfall, while the VWA represents a greater contribution from in-cloud removal (Aikawa and Hiraki, 2009;Wang et al., 2009;Xu et al., 2017). Thus, it is reasonable that the correlations are stronger for the first fraction than for the VWA, see Table 1. This indicates that the concentration of chemical ions in precipitation at the start of rainfall is more greatly influenced by aerosols below the cloud. As rainfall continues and below-cloud concentrations are reduced, there is an increased contribution from in-cloud scavenging, which is less influenced by aerosols in the surface layer. This is confirmed by the substantial difference in the two R coefficients for the cation ion Ca^{2+} (0.85 for the first fraction, 0.47 for the VWA), which often exists in coarse particles below cloud. For the fine particle SO_4^{2-} which is present both in and below clouds (Xu et al., 2017), the difference in the two R coefficients is small.

The slope of the linear fits in Figure 3 can be used to calculate the scavenging ratio H, which is the ratio of the ions concentration in precipitation (mg/L) and in air ($\mu g/m^3$). The H ratio is 0.25×10^6, 0.16×10^6 and 0.15×10^6 for SNA, SO_4^{2-}, NO_3^- and NH_4^+ respectively. This is similar to that reported for rainfall events in 2014 in Beijing

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(0.26×10^6, 0.35×10^6 and 0.14×10^6 for SNA) by Xu et al. (2017) and consistent with those estimated in the eastern United States (0.11-0.38×10^6, 0.38-0.97×10^6 and 0.2-0.75×10^6 for SNA) (Hicks, 2005). Compared with SO_4^{2-} and NH_4^+, the scavenging ratio for NO_3^- shows larger differences between this study and previous studies, corresponding to larger uncertainties to the R between the concentrations of ions in precipitation and in air for VWA in Figure 3a (lower significance $p<0.05$).

Wet deposition can affect much of the atmospheric column through in-cloud and below-cloud scavenging processes. The vertical column density (VCD) of SO_2 and NO_2 from satellite during 2000s to 2017 is used here to compare with the inter-annual variations in wet deposition in Beijing (Figure S1). Consistent variation of the VCD and the yearly VWA concentration in precipitation is found in S and N. A continuous decrease is found in VCD SO_2 from 2005 to 2017, matching the trend in SO_4^{2-} deposition, while for VCD NO_2 shows an increase from 2001 to 2011, a decrease after 2011 and little change over the preiod 2014-2017. This implies that the Action Plan not only benefits air pollutants in the surface layer but also those in the total column. Due to faster decreases in emissions of S than N (Zheng et al., 2018), the ratio of S/N in both precipitation (SO_4^{2-}/NO_3^-, μeq/L) and air (SO_4^{2-}/NO_3^-, μg/m^3) are found to decrease, with the change in ratio in precipitation at 281%, 44% and 459% during 1995-2010, 2014-2017 and 1995-2017, and in air at 48% during 2014-2017, respectively, see Figure S2. This is also consistent with the trend reported in whole China during 2000-2015 by Itahashi et al. (2018). The chemical composition of precipitation is directly related to the amount of precipitation, and as a consequence it is difficult to identify inter-annual variations in chemical concentrations. The ratio of S/N in precipitation is a useful index to investigate the relative contributions of these acidifying species. In addition, the ratio of NH_4^+/NO_3^- is investigated here and a clear decrease is found during 2014-2017 both in precipitation and in air. This indicates that NH_4^+ is decreasing faster than NO_3^-. This evidence clearly confirms that nitrate should be the major target for air pollution controls in the next Action Plan.

3.3 Proportion of below cloud scavenging

As described in section 2.3, the in-cloud ion concentration ($\bar{C}$, in Eq 1) can be derived

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279 from the exponential fit of the observed rainwater concentrations. Table 2 lists the
280 asymptote value and the exponential fitting equation of the evolution of each ion
281 concentration in precipitation with the increment of rainfall. As shown, the asymptote
282 value (here after, exponential approach) based on the median data for SO_4^{2-}, NO_3^- and
283 NH_4^+ was 3.18 mg/L, 2.32 mg/L and 1.39 mg/L, respectively. The SO_4^{2-} and NO_3^- are
284 within the range of reported in cloud concentrations for Beijing (3.33 mg/L and 2.75
285 mg/L for SO_4^{2-} and NO_3^- in Xu et al., 2017), while the NH_4^+ in this study is lower than
286 previous studies (2.51 mg/L in Xu et al., 2017 and 2.1-4.5 mg/L in Wang et al., 2009).
287 In-cloud concentrations for other ions, i.e., Ca^{2+}, F^-, Cl^-, Na^+, K^+ and Mg^{2+}, are 0.67
288 mg/L, 0.04 mg/L, 0.27 mg/L, 0.1 mg/L, 0.06 mg/L and 0.08 mg/L, respectively. For
289 comparison, the average concentration in fractions 6 to 8 (F6#~F8#) in each rainfall
290 event (here after, average approach) is used to estimate the in-cloud concentration for
291 events where successive rainwater concentrations do not show an obvious decrease or
292 where other factors such as precipitation intensity are important, see Table 2. Similar
293 results are found for most ions with the exponential and average approach except for
294 NH_4^+, F^-, K^+ and Mg^{2+}, where the maximum difference is less than 20% (Table 2). Thus,
295 the replacement of in-cloud concentration by the average value is acceptable for SO_4^{2-},
296 NO_3^-, Ca^{2+}, Cl^- and Na^+ but much uncertainty for the other ions. It is worth noting that
297 for all ions the average approach gives higher estimates of in-cloud concentrations, and
298 this can be recognized as an upper limit for in-cloud concentrations.

299 Following Eq (2), the contribution of below-cloud scavenging to wet deposition in
300 each rainfall event during 2014-2017 are estimated from the in-cloud concentration.
301 Figure 4 shows the yearly VWA of SNA and Ca^{2+} and the in-cloud and below-cloud
302 contributions. The ratio of yearly median data for below-cloud contribution to the four
303 major components is also shown in Figure 4. Benefiting from the Action Plan, the
304 below-cloud contributions of SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+} show decreases from >50%
305 in 2014 to ~40% in 2017. In 2017, the contribution of below-cloud scavenging declines
306 to lower than 40% for SO_4^{2-} and NH_4^+, but remains at 44% for NO_3^-. Over the four-year
307 period 2014-2017, the average yearly wet deposition for all ions and the below-cloud
308 wet scavenging contributions are given in Table 2. Similar to the concentrations in

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precipitation, the wet deposition of SO_4^{2-}, NO_3^-, NH_4^+ decreased from 21.5 kgS ha^{-1} yr^{-1}, 8.9 and 19.0 kg N ha^{-1} yr^{-1} during 2007-2010 (Pan et al., 2012; 2013) to 11.4 kgS ha^{-1} yr^{-1} (3.42×10^3 mg m^{-2} yr^{-1}), 6.9 and 16.7 kgN ha^{-1} yr^{-1} (3.05×10^3 and 2.15×10^3 mg m^{-2} yr^{-1}) during 2014-2017, respectively. Below-cloud scavenging contributed to almost half of total deposition estimated with the exponential approach (50~60%), higher than the average approach (40~50%).

3.4 Below cloud scavenging impacts on the aerosol

Quyang et al. (2015) reported a significant negative correlation between accumulated rainfall and $PM_{2.5}$ in air during summer time in Beijing, indicating that rainfall has a significant effect in washing out air pollution. Inter-annual observations of both rainfall and aerosol concentration have been conducted in this study. The concentrations of air pollutants generally decrease with increasing wind speed, especially from northerly and northwesterly directions (He et al., 2001;Chan and Yao, 2008;Xu et al., 2017), as cleaner air is brought from these directions when wind speeds are greater than 4 m/s (Gonzalez and Aristizabal, 2012). To avoid this influence from airmass origin, rainfall events associated with low wind speeds (< 2 m/s) have been chosen. Nine events between 2014 and 2017 have been selected to investigate the impacts of rainfall on air pollution. Under these conditions, the variation in $PM_{2.5}$ concentration can be attributed to washout effects alone. For comparison, the monthly average concentration of $PM_{2.5}$ is calculated and displayed with the hourly concentration of $PM_{2.5}$ during the selected rainy day in Figure 5. The hourly atmospheric concentration typically shows a sharp decrease as the rainfall events occur. During the event on June 26-27 2015, the $PM_{2.5}$ concentration decreased from 120 μg/m^3 before rainfall to 20 μg/m^3 after rainfall. This indicates that the rainfall has a strong cleansing effect on the air pollution. Quyang et al. (2015) reported a significant correlation between the amount of rainfall in summer in Beijing and the decrease in $PM_{2.5}$ with an R^2 higher than 0.67. Fan et al. (2019) found a similar relationship in the Yangtze River Delta, and attributed the washing effect to the amount and speed of the rainfall.

4 Factors influencing below-cloud scavenging

4.1 Rainfall type

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The rainfall over the North China Plain in summer time is usually determined by the synoptic system such as the upper-level trough or the cold vortex. The 75 rainfall events have been classified based on synoptic system according to records from the Beijing Meteorological Service (http://bj.cma.gov.cn) with 33 events associated with upper-level troughs, 23 events associated with a cold vortex and 19 events associated with other systems. Figure 6 shows the contributions of below-cloud scavenging for the two major systems. A high contribution from below-cloud scavenging is found for rainfall events associated with an upper-level trough with the median contributions for SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+} of 56.2%, 62.1%, 56.3% and 61.9%, respectively. In the contrast, the contributions during rainfall events under cold vortex conditions are significant lower, with the values of 42.2%, 44.5%, 41.7% and 53.9%, respectively. Rainfall events associated with an upper-level trough are usually accompanied by orographic or frontal precipitation and are characterized by long and continuous precipitation (Shou et al., 2000). This suggests that below-cloud scavenging of chemical components is important for this rainfall type due to air mass transport from outside Beijing. In contrast, rainfall events associated with a cold vortex usually originate from strong thermal convection and are characterized by short heavy rainfall (Zhang et al., 2008;Liu et al., 2016;Zheng et al., 2020). This is common during the summer months in Beijing with deep convective clouds (Yu et al., 2011;Gao and He, 2013), and suggests that there is a large contribution from in-cloud scavenging to the total wet deposition.

4.2 Precipitation intensity and rainfall volume

To illustrate the impacts of rainfall on below-cloud aerosol scavenging, the relationship between the below-cloud fraction and the rainfall volume and precipitation intensity are investigated, see Figure 7. Negative correlations in below cloud fraction are found for both the rainfall volume and precipitation intensity, although the relationship with the former is stronger (R: 0.63~0.93 vs. 0.03~0.64). This is consistent with results for 2014 in Beijing reported by Xu et al. (2017). Atmospheric particles are efficiently removed below cloud by washout at the beginning of precipitation events (almost 70% of SNA is removed in the first 2-3 fractions, as shown in Figure 1). As the rainfall progresses, in-cloud rainout makes an increasingly important contribution as below-cloud aerosol

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concentrations fall. Xu et al. (2017) found that heavy summertime rainfall events with more than 40 mm of rainfall usually occur over very short periods of time, usually 2-3 h. This heavy rainfall leads to the scavenging of aerosols in a relatively localized region and prevents the compensation associated with transport of air pollutants from outside the region during longer-duration light rainfall events. This contributes to the decreased contribution of washout processes during the high intensity rainfall events.

5 Conclusions

This paper presents an analysis of below-cloud scavenging from four years of sequential sampling of rainfall events in Beijing from May of 2014 to November of 2017. The concentration of ions in precipitation varied dramatically, with yearly volume weighted averaged concentrations of SO_4^{2-}, NO_3^-, $NH_4^+$and Ca^{2+} decreasing by 39%, 12%, 25% and 35% between 2014 and 2017, respectively. Due to faster decreases in SO_4^{2-} than NO_3^- both in precipitation and in the air during the observation period, there is a significant decrease in S/N ratio in precipitation at 44% and in air at 48%. Benefiting from the national Air Pollution Prevention and Control Action Plan, the sulfur has been further reduced, while the nitrogen, especially nitrate, needs further attention in the next Action Plan to prevent deterioration of the environment associated with acid rain and photochemical pollution.

A new method has been developed and employed to estimate the below-cloud contribution to wet deposition in Beijing. The new approach suggests that the contribution from below-cloud scavenging is greater than that estimated applying simpler approaches used in previous studies. Overall, the contribution of below-cloud scavenging to the wet deposition of the four major components is important at 50~60%, with the highest contribution for NH_4^+ at 65% and lowest for SO_4^{2-} at 50%. The contribution of below-cloud scavenging shows a decrease over the period 2014-2017 for Ca^{2+}, SO_4^{2-} and NH_4^+, but little change for NO_3^- during 2015-2017. Below-cloud scavenging also has a strong cleansing effect on air pollution, and the hourly concentration of $PM_{2.5}$ is found to decrease sharply as the rainfall events occur, even with the effects from wind swept out have been accounted for.

Rainfall types also influence the contribution of below-cloud scavenging. Seventy-

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five rainfall events during the four-year periods were classified based on the local synoptic conditions. Lower contributions from below-cloud scavenging (~40%) are found for the four major ions in rainfall events associated with a cold vortex, while higher contributions (~60%) occurred associated with an upper-level trough. Precipitation volume and intensity both show a negative correlation with the below-cloud fraction. This suggests that atmospheric particles are efficiently removed via washout processes at the beginning of precipitation events. As the event progresses, rainfall in the later fractions shows a greater contribution from in-cloud rainout processes as aerosols in the surface layer have already been scavenged. To better understand the mechanism of washout processes, high resolution of measurement both in precipitation and in the air especially at the beginning of rainfall events are needed in the future.

Acknowledgment

We appreciate CNEMC for providing the data of the 6 criteria pollutants in Beijing. We also appreciate Beijing Municipal Environmental Monitoring Center for providing the aerosol components data in Beijing. This work is supported by the National Natural Science Foundation of China (Grant No 41877313, 91744206, 41620104008), Priority Research Program (XDA19040204) and the Key Deployment Program (ZDRW-CN-2018-1-03) of the Chinese Academy of Sciences.

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625

626 Table 1. Correlation of the concentrations of major ions in air in the six hours before
627 rainfall with those in precipitation. Pearson correlation coefficients are presented for
628 monthly volume weighted average (VWA) concentrations and for the first fraction ($F1^{\#}$)
629 in each event.

	SO_4^{2-} (n=13)	**NO_3^- (n=14)**	**NH_4^+ (n=13)**	**Ca^{2+} (n=9)**
VWA	0.70^a	0.53^b	0.65^a	0.47
$F1^{\#}$	0.76^a	0.62^a	0.77^a	0.85^a

630 Note: "a" and "b" represent significant correlations at $p<0.01$ and $p<0.05$, respectively.
631
632

633 Table 2. Exponential fitting for the concentrations of major ions in different fractions of rainfall, and the contribution of below-cloud scavenging
634 to total deposition.

Chemical components	Exponential Fitting for 50th percentile[a]	R^2 (n=11)	Intercept (mg/L)	Below cloud %[b]	Average of F6#-F8# (mg/L)	Below cloud %[c]	Difference %[d]	Total wet deposition (mg/m^2/yr)
SO_4^{2-}	$y=3.17+10.28\ e^{-0.51x}$	0.85	3.18	50%	3.33	48%	<3%	3423.3
NO_3^-	$y=2.32+11.03\ e^{-0.45x}$	0.81	2.32	59%	2.59	54%	<6%	3046.5
NH_4^+	$y=1.39+5.81\ e^{-0.28x}$	0.79	1.39	65%	1.95	51%	<9%	2149.5
Ca^{2+}	$y=0.67+6.81\ e^{-0.6x}$	0.93	0.67	52%	0.72	48%	<6%	746.0
F^-	$y=0.04+0.24\ e^{-0.34x}$	0.91	0.04	56%	0.05	40%	<10%	49.0
Cl^-	$y=0.27+2.2\ e^{-0.6x}$	0.95	0.27	53%	0.29	50%	<5%	309.7
Na^+	$y=0.1+1.34\ e^{-0.94x}$	0.91	0.10	64%	0.10	64%	<1%	150.6
K^+	$y=0.06+0.49\ e^{-0.47x}$	0.89	0.06	64%	0.07	58%	<9%	89.8
Mg^{2+}	$y=0.08+0.81\ e^{-0.4x}$	0.83	0.08	61%	0.11	46%	<13%	109.2

635 [a] fitting for the median of each fraction in different rainfall events; [b] below cloud portion calculated based on the fitting curve; [c] below cloud portion
636 calculated based on the average value of fractions 6 to 8 (F6#~F8#) in rainfall events; [d] difference in concentrations between adjacent 1 mm
637 increments after 5 mm accumulated precipitation.
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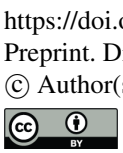

Atmospheric Chemistry and Physics Discussions

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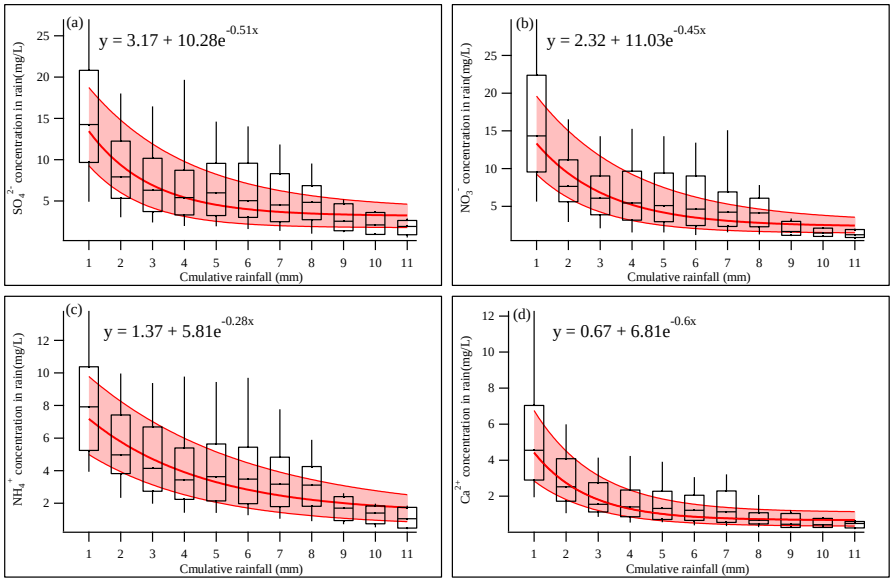

641

642 Figure 1. Concentrations of SO_4^{2-} (a), NO_3^- (b), NH_4^+ (c) and Ca^{2+} (d) in each 1-mm
643 fraction of rainfall (i.e., F1#, F2#, …) over different rainfall events in the observation
644 periods. The red line shows an exponential fitting using the 50th percentile of the data
645 and the red shading indicates the range between the 25th and 75th percentiles.

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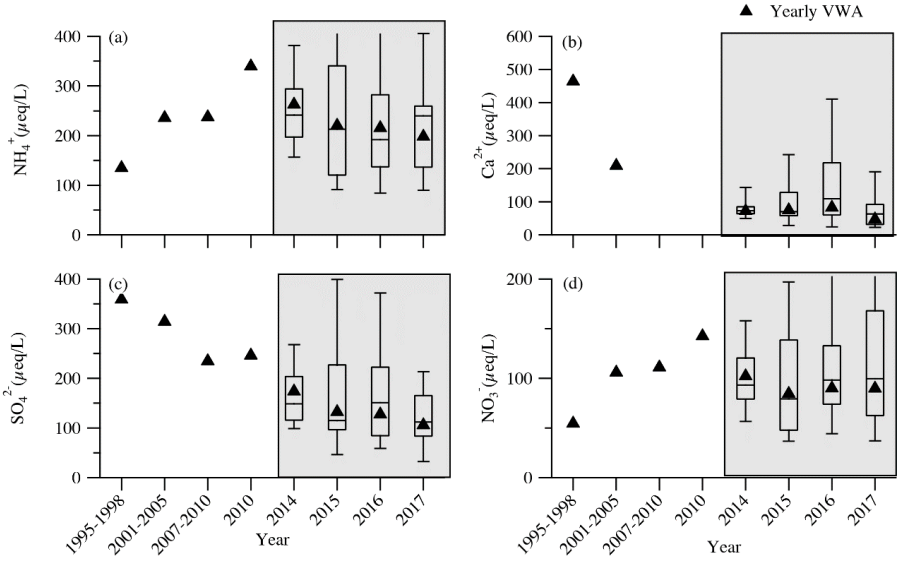

648

649 Figure 2. Time series of annual volume weighted average (VWA) concentration of the
650 four major components NH4+ (a), Ca^{2+} (b), SO_4^{2-} (c) and NO_3^- (d) in precipitation in

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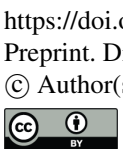

Atmospheric Chemistry and Physics Discussions

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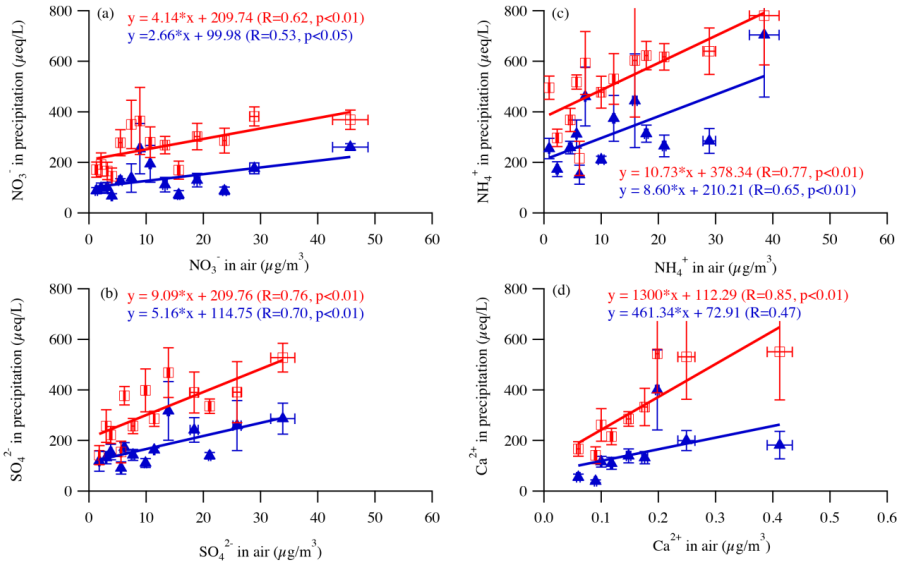
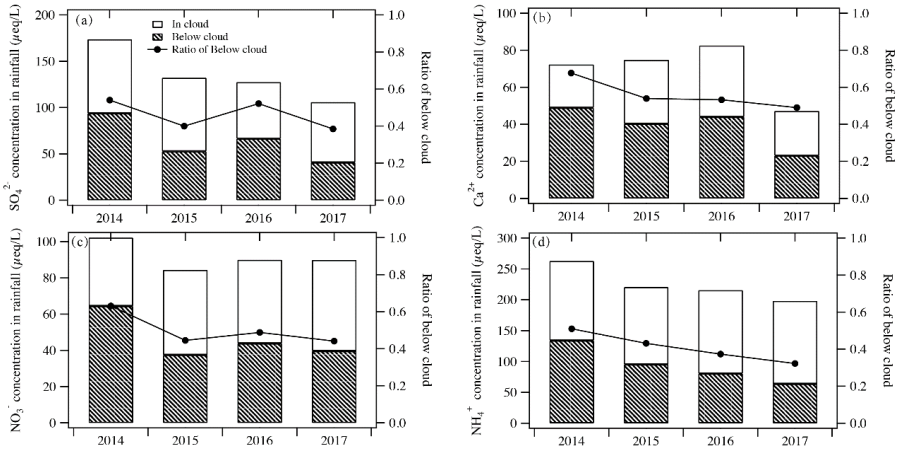


653

654 Figure 3. Relationships between the concentration of NO_3^- (a), SO_4^{2-} (b), NH_4^+ (c) and
655 Ca^{2+} (d) in precipitation and in air in the 6 h before each precipitation event. The red
656 square and blue triangle represented the relationships between the concentration of ions
657 in air with that in F1# and in VWA, respectively.



658

659 Figure 4. The annual volume weighted average below-cloud and in-cloud portion of
660 SO_4^{2-} (a), Ca^{2+} (b), NO_3^- (c), and NH_4^+ (d) during 2014-2017. The ratio of annual
661 median below-cloud contribution for each component is represented as the black line
662 in each panel.

663

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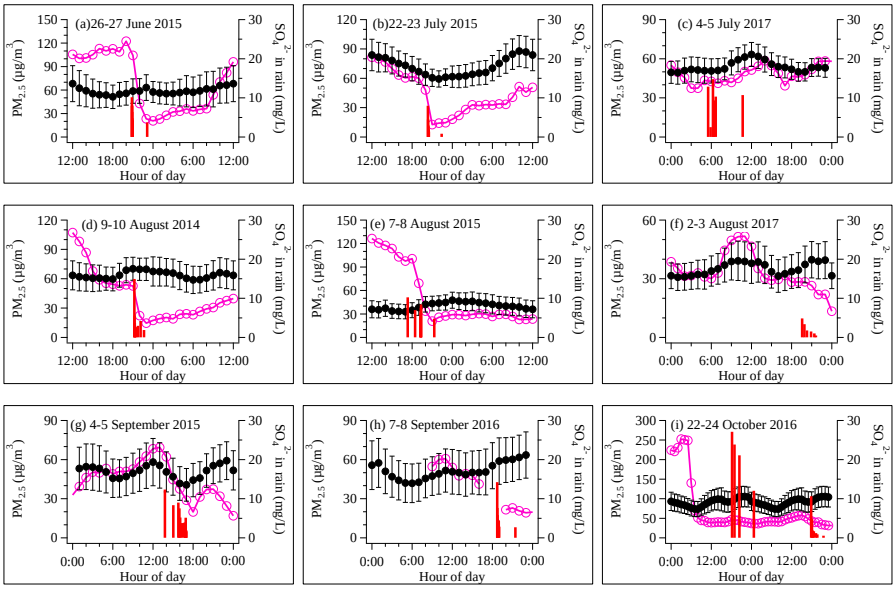

Figure 5. Diurnal variations in hourly mean $PM_{2.5}$ concentrations (pink line with unfilled circles) during specific rainfall events and on other days in the corresponding month (solid black circles with σ/3 error bars) along with the sulfate ion concentration in rainfall (red bars).

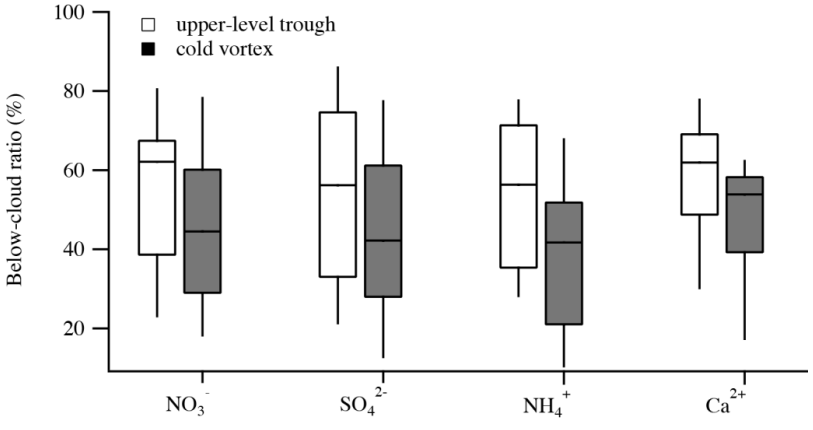

Figure 6. Contribution of below-cloud scavenging during rainfall events associated with different synoptic conditions.

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Preprint. Discussion started: 27 November 2020

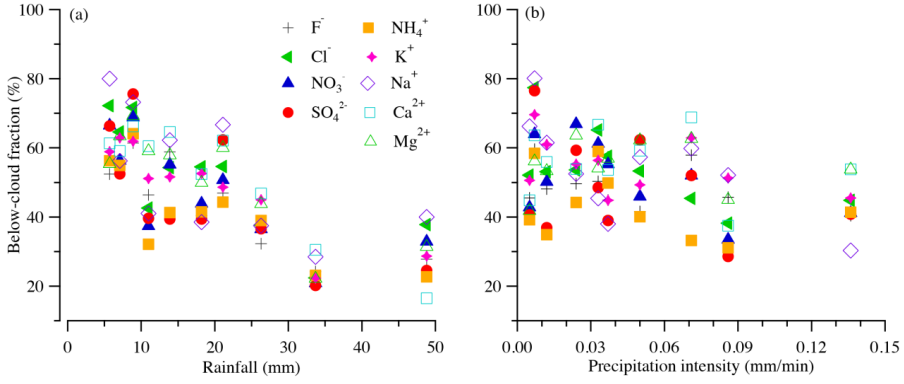

Figure 7. Contribution of below-cloud scavenging in events with different rainfall volume and precipitation intensity