

The authors provided a thoughtful response to the major comments. However, some of the information was not incorporated into the paper. To achieve a more balanced discussion on wet deposition of S and N, it is important to discuss in the paper whether wet scavenging of coarse particles and gas-phase S and N compounds are important or not and provide justification. Also, the theoretical explanation on below-cloud and in-cloud scavenging should be included in the paper to support the method used to estimate below-cloud and in-cloud scavenging contributions. Below are some of the specific comments that were partly addressed in the responses but not in the revised paper. Providing additional explanations in the paper would help improve its scientific quality.

[Response]: We appreciate the valuable comments of the anonymous referee. We have prepared the point-by-point responses to address the reviewer's comments as shown below. The additional explanations were added in the revised manuscript.

Response to “*To achieve a more balanced discussion on wet deposition of S and N, it is important to discuss in the paper whether wet scavenging of coarse particles and gas-phase S and N compounds are important or not and provide justification.*”

First, since the ions collected in precipitation are both from fine and coarse particles as well as the gas phase S and N compounds, the effect of coarse particles and gas phase S and N compounds have been considered in calculating the proportions of in-cloud and below-cloud scavenging to total wet deposition. However, the proportions estimated based on measurements cannot be distinguished from the effects of particles or gaseous compounds. The model study in Japan showed consistent fractions of in-cloud and below-cloud scavenging to total wet deposition between simulated and observed values, except one site, where is the region of high emission flux of SO₂. In this region, the simulated below-cloud scavenging contribution was apparently greater than the observed results. Specifically, the model shows the SO₂ and HNO₃ gases dominantly contributed to the below-cloud scavenging of SO₄²⁻ and NO₃⁻ in the regions of high emission flux of SO₂, in while the aerosol removal was dominated by the in-cloud scavenging process. In their model set up, all of below-cloud gas SO₂ was assumed to be dissolved into raindrop and be fully oxidized to SO₄²⁻. However, as suggested by Seinfeld and Pandis (2006), the aqueous equilibrium between ambient gas and precipitation cannot be assumed due to the relatively short residence times of falling precipitation. Thus, the assumptions used in Kajino et al. (2015) might overestimate the contribution of gas SO₂ to below-cloud scavenging. Besides, considering the large amounts of particles (60-90 μg/m³ in mass concentration) below-cloud in Beijing, the gases compounds may be not as important as that in simulation in Japan. According to the yearly book of “*Environmental Bulletin in Beijing*” from 1994 to 2017, the yearly concentration of SO₂ has a dramatically decreasing from 26.5 μg/m³ in 2013 to 8 μg/m³ in 2017. This relatively low-level concentration of SO₂ at surface may not contribute a dominant role in wet deposition of SO₄²⁻. Similar case in NO₃⁻, the ratio of gas-phase HNO₃ and the total NO₃⁻ in the summer in Beijing is only 0.12 according to the measurement study of Yue *et al.* (2013). The fraction of total inorganic nitrate as particulate nitrate instead of gaseous nitric acid over the NCP increased from 90% in 2013 to 98% in 2017 (Zhai et al., 2021), which means the gaseous nitric acid has been consumed by high level of ammonia concentrations. We assumed the 10% ratio of gases

added into the washout process, which only leads to less 5% difference of below-cloud scavenging contribution to total wet depositions. Anyway, for NH_3 , there might be larger uncertainties, since the high concentration of NH_3 at ground surface over NCP (Pan et al., 2018). Kasper-Giebl et al. (1999) reported that 49-79% of NH_4^+ in precipitation are from particulate ammonium, which indicate the large uncertainties of contribution from gases still exists in the form of NH_4^+ wet deposition. The uncertainties are mainly from the indistinct window for the in-cloud scavenging judgement due to high concentration of gas NH_3 at ground surface which is not easy to be scavenged completely during the short time fraction measurements. This is also confirmed by the larger difference in below-cloud contribution to NH_4^+ wet deposition than other ions estimated by the exponential approach and the average approach in Table 2.

Second, in discussion the relationships between precipitation and ambient air concentrations of inorganic ions, only components in $\text{PM}_{2.5}$ are included. Due to the absent of the on-line observed coarse particles and gas phase N compounds, the relationships as well as the scavenging ratio W may exist certain uncertainties. These uncertainties have been evaluated in the revised manuscript. For S, we added gas SO_2 to testified its role to the relationships. Figure 1 shows the Relationships between the concentration of SO_4^{2-} in precipitation and in air (SO_4^{2-} in precipitation vs SO_4^{2-} , and SO_4^{2-} in precipitation vs $\text{SO}_2+\text{SO}_4^{2-}$). The correlation coefficients R increased if the role of gas SO_2 was considered (R of SO_4^{2-} in precipitation vs SO_4^{2-} is 0.7, and R of SO_4^{2-} in precipitation vs $\text{SO}_2+\text{SO}_4^{2-}$ is 0.75). However, the scavenging ratio W was not changed, with the difference lower than 1%. For N, the contribution of gaseous HNO_3 to total inorganic nitrate is less than 2% in NCP according to Zhai et al. (2021), which can be ignored in this study. According to more than one-year measurements in Beijing (Tian et al., 2016), SO_4^{2-} , NO_3^- and NH_4^+ in coarse particles account for 18%, 27% and 10%, respectively. The lower coefficient R in NO_3^- than SO_4^{2-} and NH_4^+ in Figure 4 is attributed to the absent of considering NO_3^- in coarse particles. Besides, due to high concentration of NH_3 at ground surface over NCP (Pan et al., 2018), the NH_4^+ in precipitation from gaseous NH_3 cannot be ignored (Kasper-Giebl et al., 1999). The ratio of $\text{NH}_4^+/(2\text{SO}_4^{2-}+\text{NO}_3^-)$ in precipitation and in $\text{PM}_{2.5}$ was calculated. The lower ratio in precipitation than that in $\text{PM}_{2.5}$ was found, with 0.95-1.01 in precipitation and 1.35 in air. This implicated the impacts of rich gas NH_3 at ground surface going into the precipitation by reacting with gaseous HNO_3 and forming as NH_4NO_3 after $(\text{NH}_4)_2\text{SO}_4$. Thus, the contribution of coarse particles and gases to the relationships of S and N compounds in precipitation and the atmosphere is not as important as the fine particles, except NO_3^- in coarse particles and the gaseous NH_3 , which should be considered in the future.

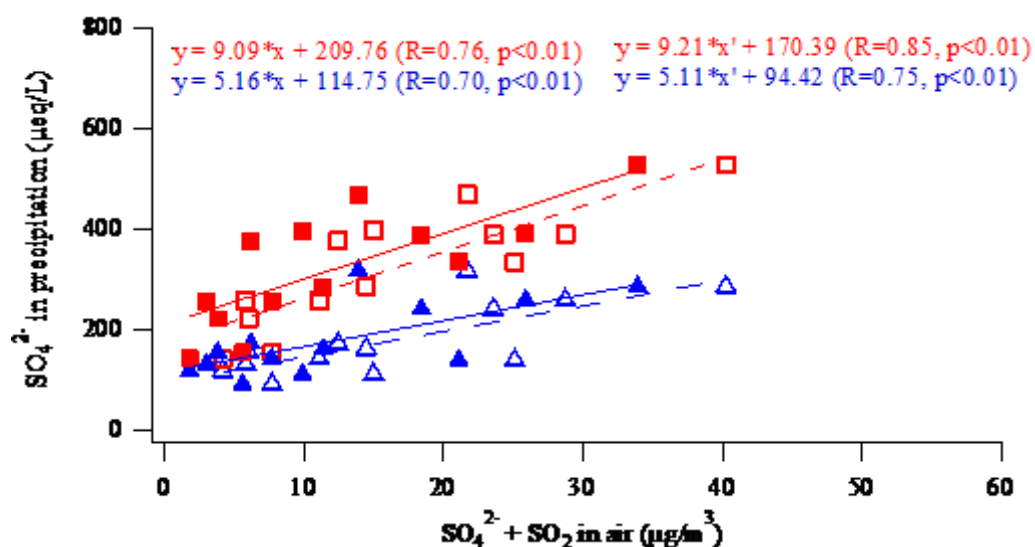


Figure 1. Relationships between the concentration of SO_4^{2-} in precipitation and in air in the 6 h before each precipitation event. The solid (hollow) red square and blue triangle represented the relationships between the SO_4^{2-} concentration ($\text{SO}_4^{2-} + \text{SO}_2$) in air with that in F1# and in VWA, respectively. The solid and hollow lines represented linear regression line of SO_4^{2-} in precipitation and in air as well as that of SO_4^{2-} in precipitation and $\text{SO}_4^{2-} + \text{SO}_2$ in air.

Response to “Also, the theoretical explanation on below-cloud and in-cloud scavenging should be included in the paper to support the method used to estimate below-cloud and in-cloud scavenging contributions.” The theoretical explanation on below-cloud and in-cloud scavenging have been included in the revised manuscript. For more details, please see the response to specific comments 4.

L22-24: Why would the Action Plan result in declines in Ca^{2+} given that it is mainly derived from crustal emissions? - This needs to be explained in the paper.

[Response]: It has been explained in section 3.1 of the revised manuscript as: *The significant declines in VWM concentration of Ca^{2+} is found in precipitation with the decreases rate as 36.1% yr-1 in 1995-2010 and 8.8% yr-1 in 2014-2017. The emission and the concentration data of Ca^{2+} are absent in this study. Instead, the different of PM_{10} and $\text{PM}_{2.5}$ ($\text{PM}_{10} - \text{PM}_{2.5}$) concentration during 2013-2017 have been calculated to represent the coarse particles, in which the Ca^{2+} compound is mainly loaded. The results show that the concentration decreased from 31.2 $\mu\text{g}/\text{m}^3$ in 2013-2014 to 24.0 $\mu\text{g}/\text{m}^3$ over 2015-2017. This indicates the improvement of coarse particles even which is derived from crustal emissions have been made through the Action Plan. As that is mentioned above, the Action Plan including emission reduction not only from energy consumption of industry but also the fugitive dust in cities, which should result the decline in Ca^{2+} .*

L30: Was there a continuous year-to-year decline in the percentages, i.e. in 2015 and 2016? If so, this should be stated. If not, the next sentence, which suggests the result is

due to the Action Plan, should not be included in the abstract because there is no clear decreasing trend. - In the response, the authors stated there was an overall decline but not a year-to-year decline in the percentages. If there is no year-to-year decline, the percentage decreases from 2013 to 2017 are likely not statistically significant.

[Response]: Thanks for the comment. Although there is not a continuous year-to-year decline in the percentages, the statistically significant ($p > 0.01$) decreasing trend have been observed in PM_{2.5} concentration and the major ions in precipitation except NO₃⁻ after the Action Plan launched in 2013. Thus, the expressions on the Action Plan in the next sentence are kept in the abstract.

L78-80: Each precipitation event is unique in terms rainfall intensity, droplet sizes and distribution, precipitation form (rain, snow, or sleet), air concentrations of chemical components, etc. Meteorology varies with location; some locations are frequently affected by thunderstorms or deep convective scavenging. Can you address whether these factors are taken into consideration when using the sequential precipitation sampling method to estimate in-cloud or below-cloud scavenging contributions? - These uncertainties should be discussed in the paper because it is not clear how these factors affect wet scavenging and the proportions from in-cloud and below-cloud processes.

[Response]: Thanks for the comment. The unique characterization of each precipitation event was considered in calculation of the proportions from in-cloud and below-cloud processes, as the exponential approach to each unique event was made. The variations of the ions concentration in each fraction of each rainfall are influenced by the synthetic effects of meteorology conditions. After the estimation of the proportions of below-cloud scavenging in each precipitation event, the uncertainties from the meteorology conditions have been discussed in section 4 “*Factors influencing below-cloud scavenging*”. In the section, the influence of these factors affecting wet scavenging were investigated through the correlation analysis between below-cloud proportions with the rainfall type as well as the rainfall intensity. The below-cloud proportions varied from 20% to 80% among the 69 rainfall events. Among these rainfall events, three types of precipitation such as cold vortex, upper-level troughs and others have been classified, based on the records of synoptic system from the Beijing Meteorological Service. A high contribution from below-cloud scavenging is found for rainfall events associated with an upper-level trough, while a lower contribution during rainfall events under cold vortex conditions. In addition, the negative correlations in below cloud fraction are found for both the rainfall volume and precipitation intensity. The heavy rainfall is corresponding to the decreasing of below-cloud proportion. The more detailed explanation was made in section 4.1 and 4.2 of the paper. To make this discussion more clearly, a description was added in the beginning of section 4 in the revised manuscript. The description is as: *Each precipitation event is unique in terms rainfall intensity, droplet sizes and distribution, rainfall type (thunderstorms or deep convective scavenging), air concentrations of chemical components, etc. The unique characterization of each precipitation event was considered in calculation of the proportions from in-cloud and below-cloud processes, as the exponential approach to*

each unique event was made. The below-cloud proportions varied from 20% to 80% among the 69 rainfall events. The influence of these factors affecting wet scavenging were investigated through the correlation analysis between below-cloud proportions with the rainfall type as well as the rainfall intensity.

L141-147: One initial criticism I have on this assumption is why below-cloud and in-cloud processes have to occur one after another instead of simultaneously. A full justification is necessary given that the major results of this study depend on this analysis and interpretation. – The theoretical explanation that was provided in the response should be addressed in the paper as well.

[Response]: Thanks for the comment. The theoretical explanation was added in the section 2.3 of the revised manuscript. The text is as: *According to (Seinfeld and Pandis, 2006), species can be incorporated into cloud and raindrops inside the raining cloud and this process determine the initial concentration of raindrops before they start falling below the cloud base. In this stage, despite of the efficient process of the nucleation scavenging in cloud, the total mass of aerosol in cloud is almost stable due to the slow process of interstitial aerosol collection by cloud droplets which is the determination process to aerosol mass. That is to say, the initial concentration of raindrops in cloud is well mixed and can be considered as a stable statue during the whole rainfall event. That is why many observations in different regions (Aikawa et al., 2009; 2014; Wang et al., 2009; Quyang et al., 2015; Xu et al., 2017) reported that the chemical components in a rainfall event show a decayed variation with the increase of precipitation amount and eventually tends to a stable and low concentration level. The assumption in this study as well as the previous studies is based on this fact. It does not mean the below-cloud and in-cloud scavenging occur in sequence. But, instead, the two processes have been mixed in all stage of the rainfall event with the below-cloud scavenging contributed more in beginning fraction and the in-cloud scavenging contributed more in the later fraction due to the depletion of the air pollutants below cloud by washout.*

Section 3.1: Why are the results of other inorganic ions not discussed? For a better understanding of the impacts of acidification on ecosystems, wet deposition fluxes should be presented as well. While there may be significant decreases in VWM concentrations, interannual variability in precipitation amounts may result in less significant decreases in wet deposition fluxes. - The paper did not discuss the results for Na⁺, K⁺, Mg²⁺, Cl⁻ and F⁻, which were measured in the study as stated in the methodology. There was also no discussion on the wet deposition fluxes and how changes in the precipitation amounts can affect trends in the wet deposition fluxes.

[Response]: Thanks for the comment. In this study, only the major ions in precipitation are considered. According to the measurement, the two anions (SO₄²⁻ and NO₃⁻) and two cations (NH₄⁺ and Ca²⁺) are discussed in the main text with the other ions listed in Table 2 and plotted in Figure 7 in the revised manuscript. As for the wet deposition, the fluxes have been added in Figure 2. The corresponding description in the paper Section 3.1 is as: *For a better understanding of the impacts of acidification on ecosystems, wet*

deposition fluxes of the four major ions in precipitation are also plotted in Figure 2. Similar variations are found as that presented in VWA of the four major ions. Observations on S and N wet deposition (Pan et al., 2012; 2013) during 2007-2010 show the value of 21.5 kg S ha⁻¹ yr⁻¹ and 27.9 kg N ha⁻¹ yr⁻¹ (19.7 and 8.2 kg N ha⁻¹ yr⁻¹ through NO₃⁻ and NH₄⁺) in Beijing, respectively. Compared with those results, significant decreases (11.4 kg S ha⁻¹ yr⁻¹ and 23.6 kg N ha⁻¹ yr⁻¹) were observed in the four-years measurements during 2014-2017 in this study.

Section 3.3: An exponential curve was used to fit the data points and then the horizontal asymptote was used to determine the precipitation concentration representative of rainout. One issue that I have with this approach is that there were only 11 data points or precipitation fractions. Previous studies (e.g. Aikawa and Hiraki, 2009) that conducted sequential sampling of precipitation found that the precipitation concentrations could increase in the much latter fractions of precipitation. It seems that more precipitation fractions need to be collected in order to observe what happens to the precipitation concentrations. – Based on the responses, the authors agree that longer fraction measurements and more detailed analysis on the uncertainties are needed in the future. This should be mentioned in the paper.

[Response]: Agree. It was mentioned in first paragraph of section 3.3 of the revised manuscript as: *It is also important to note that the increased concentrations of ions in the latter fractions were observed in few events in this study. This may due to the unique meteorological conditions (i.e., rainfall type, rainfall intensity) and air pollutants movement during each precipitation. Thus, despite the longer precipitation fractions in this study were collected, more longer fraction measurements and more detailed analysis on the uncertainties are needed in the future. The influences of meteorological conditions (i.e., rainfall type, rainfall intensity) are discussed in section 4.* It was also mentioned in last sentence of the second paragraph of section 3.3 in the revised manuscript as: *As it mentioned above, more longer fraction measurements as well as the influence of NH₃ to NH₄⁺ wet deposition are needed in the future.*

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