

# ***Interactive comment on “Inter-annual variations of wet deposition in Beijing during 2014–2017: implications of below-cloud scavenging of inorganic aerosols” by Baozhu Ge et al.***

## **Anonymous Referee #2**

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This study analyzed concentrations of sulfate, ammonium, nitrate and other inorganic ions in precipitation and fine PM and estimated the fraction of the wet deposition attributed to in-cloud and below-cloud scavenging processes. The sequential sampling of precipitation over the course of a precipitation event provides interesting insight into changes in the precipitation chemistry that cannot be obtained from daily or weekly precipitation monitoring that are reported in many studies. The study introduced a newer approach to estimate the in-cloud and below-cloud wet scavenging proportions. In spite of the novel aspects in this study, the scientific discussions on wet scavenging of acidifying pollutants needs to be improved.

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The results and discussion center on the wet scavenging of inorganic ions in PM<sub>2.5</sub>. There was hardly any discussion on the wet scavenging of coarse particles and gas-phase S and N compounds that can also contribute substantially to wet deposition of sulfate, nitrate and ammonium. The paper discussed relationships between precipitation and ambient air concentrations of inorganic ions; however, the latter was based on components in PM<sub>2.5</sub>. How would the relationship change if coarse PM and gas-phase compounds were included? Similarly for the below-cloud scavenging results, there needs to be a more balanced discussion on particle and gas-phase scavenging.

A more detailed explanation as to why the beginning and latter precipitation fractions represent below-cloud and in-cloud scavenging, respectively, is necessary since most of the results from this study are based on this key assumption. This data analysis method seems to assume that below-cloud and in-cloud scavenging have to occur in sequence.

The discussion on temporal variations in precipitation concentration of inorganic ions is lacking some depth. Further analysis with annual emissions data are necessary to explain interannual changes and appreciate the impact of the air pollution control policies implemented.

The way the below-cloud percentages are reported in the paper raises some critical questions. In this version, only the median below-cloud percentage were reported. It is uncertain how representative are the median values considering that each precipitation event is unique in terms of rainfall intensity, precipitation form (rain, snow, or sleet), air concentrations of chemical components, type of weather system, etc. It is important to state or discuss under what conditions apply to those below-cloud percentages and their limitations. A range of the below-cloud percentages should also be included as well as some discussion on the variability of the below-cloud scavenging percentages.

Specific comments: L22-24: Why would the Action Plan result in declines in Ca<sup>2+</sup> given that it is mainly derived from crustal emissions?

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L25: “An improved sequential sampling method...” This is vague. The improvement to the method needs to be clarified in the abstract. It is not the improvement to the sequential sampling method that is described in the paper, but rather the improvement to the method of estimating the below-cloud scavenging proportion.

L27: Suggested revision, “below-cloud scavenging accounts for one half to two thirds of wet deposition”. To be more concise, only the second part of the sentence is necessary because it is very similar to the first part of the sentence.

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.

L36-37: “...clearly identifies oxidized nitrogen species as a major target for future air pollution controls.” This statement seems to be based only on the lack of declining trends in airborne and precipitation nitrate. The observed concentrations of nitrate also need to be considered compared to other N or S compounds. In precipitation, it seems that the VWA of nitrate was similar to that of sulfate and ammonium was even higher than nitrate. It is not clear why the policy recommendation is to target oxidized nitrogen and not other N or S compounds as well.

L44-46: Do these factors affect below-cloud rain scavenging only or both rain and snow?

L57-58: For which chemical components do these results apply to? Can you provide details on the modeled and measured scavenging coefficients?

L60-64: Here you argue that uncertainties in below-cloud scavenging coefficients is a potential reason for model underestimation of nitrate and sulfate wet deposition. How important are other sources of model uncertainties, such as N and S emissions, chemical transformation, changes in other ambient N and S compounds, etc.?

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L78-80: “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”. The wording is confusing. Why does the latter precipitation increments in sequential sampling represent in-cloud scavenging, while the start of the precipitation increments represent below-cloud scavenging? At what point during a precipitation event does the dominant wet scavenging process change from below-cloud to in-cloud? Is this transition point the same for all precipitation events and locations? 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?

L105: How much precipitation is collected in the eighth fraction? These details should be included in the paper.

L109: In the 69 full events, what were the total precipitation amounts collected? Are they roughly the same for each event or do they vary greatly? At what point do you have to conduct manual sampling to collect the remainder of the precipitation? These details should be included in the paper.

L141-147: Is there additional evidence that can be presented to justify the assumption that precipitation at the start of an event represents below-cloud scavenging while latter precipitation represents in-cloud scavenging? Some studies have measured concentrations of chemical components in cloud water as an indication of in-cloud scavenging; however, the method in this study are based solely on the precipitation at the surface. 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.

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L157: In previous studies, it seems that the 5 mm accumulated precipitation cut-off was based on the point where there was a lack of change in the precipitation concentrations. This is not entirely subjective.

L164-174: Clarity on the methodology is needed. You mentioned that each precipitation event is unique in terms of the decreasing rate in the precipitation concentrations. What is the reason for combining all the precipitation events prior to fitting a regression curve? Why not fit a curve for each event? What is the purpose of fitting the data through the first and third quartiles – can this serve as an estimate of the uncertainties? “In theory, the concentration of chemical ions stabilize at higher rainfall increments and this represents the concentration in cloud.” A brief explanation of the theory should be provided in the paper.

Equations 1,2: What does n represent? n in eq. 1 is different from the n in eq. 2.

L185: Some background information on the Action Plan is needed in the introduction to understand what effects these policies may have on air quality. Which pollutants does the Action Plan target and what was implemented?

Section 3.1: Why are the results of other inorganic ions not discussed? The annual changes in the VWM concentrations should be discussed with changes in emissions of the precursor pollutants, such as SO<sub>x</sub> and NO<sub>x</sub> emissions, and policies that were introduced to manage those emissions. There should also be more discussion on what was causing the significant declines in sulfate and Ca<sup>2+</sup> in the earlier period. Air pollution control measures typically target major anthropogenic contaminants, but here you have shown significant decreases in Ca<sup>2+</sup> which is largely from soil emissions. It is not clear how the Action Plan played a role in the reduction of VWM Ca<sup>2+</sup>. 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.

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L219: H usually denotes a Henry's Law constant. It is more suitable to use W or SR to denote scavenging ratios as this is consistent with literature.

L234: "while the VWA represents a greater contribution from in-cloud removal..." It was stated earlier that latter fractions of the accumulated precipitation represents in-cloud removal. Why was the VWA concentrations (which may include below-cloud and in-cloud contributions) used instead of the concentrations in the latter precipitation fractions?

L237-238: "This indicates that the concentration of chemical ions in precipitation at the start of rainfall is more greatly influenced by aerosols below the cloud." This conclusion is not correct because the scavenging of acidic gases like HNO<sub>3</sub> and SO<sub>2</sub> can also contribute to nitrate and sulfate in precipitation. Another issue with the correlation analysis between precipitation and air concentrations (in Fig. 3) is that only fine aerosols were considered. Would there be any changes to the correlation results if acidic gases and coarse aerosols were included?

L245: The scavenging ratios of SNA do not include coarse particles since only PM<sub>2.5</sub> chemical composition were measured. It also does not include the wet scavenging of acidic gases. This needs to be mentioned in the paper because typically scavenging ratios take into account all the chemical species in air that can undergo wet deposition. It seems that the scavenging ratios of SNA calculated in this study is not an accurate reflection of the wet scavenging efficiency of SNA.

L264-266: The percentages should be converted to annualized percentages. Some of the time periods are much longer than others, which makes it appear that the rate of decrease is larger.

L269: "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." This statement is incorrect. There are other factors affecting the precipitation chemistry besides the precipitation amount. Section 3.3: An exponen-

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tial 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.

L303-308: “Benefiting from the Action Plan, the below-cloud contributions. . .” This part may not be necessary because it was discussed earlier that the policies in the Action Plan help reduced the VWM of inorganic ions. The Action Plan did not directly affect the below-cloud scavenging process. Rather, it improved the air quality which in turn decreased the VWM concentrations.

Section 3.4: I think this section is not necessary because the findings are not substantially new from what has already been discussed in the paper. Here you are showing the effects of rainfall on ambient air sulfate. The washout effects were already discussed in Figure 1, which shows the decrease in VWM concentrations of the inorganic ions with increasing rainfall.

L392: “highest contribution for  $\text{NH}_4^+$  at 65% and lowest for  $\text{SO}_4^{2-}$  at 50%”. This was stated in the conclusion and abstract, but was not elaborated in the results. I expected the highest contribution to below-cloud wet scavenging would have been from  $\text{Ca}^{2+}$  or  $\text{Na}^+$  given that they are predominantly associated with coarse particles and locally emitted.

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