Response to Anonymous Referee #1's Comments

First of all we thank the reviewer for his valuable suggestion on our study and sincerely appreciate the reviewer's insightful and helpful comments.

Below we explicitly respond to each of the items raised in the comments by anonymous referee #1. These comments are indicated in **bold**, whereas the author's response is presented in blue and revisions in red in revised manuscript.

R1C1:

The authors present an analysis of atmospheric ammonia over South and East Asia based on the MOZART-4 model that is driven by the HTAP-v2 emission inventory. Model results are compared against IASI satellite observations (total column), as well as surface observations of CPCB (India) and NNDMN (China) for the year 2010. This topic is very important, since ammonia partitions into the only ubiquitous volatile cation, i.e., ammonium (NH_4^+). NH_4^+ plays a crucial role in air quality and visibility due to its volatility and ability to neutralize acidic air pollutants, which are often of anthropogenic origin. And despite the various air pollution abatement efforts, ammonia concentrations are increasing in many regions of the world and are thus still of concern, not only in Asia. Despite some fundamental weakness in the modelling approach (which is unfortunately common to most such modeling studies and therefore is not a reason for rejection), this study is overall sufficiently sound. I would therefore recommend publication, if the authors take the following comments and discussion points into account.

> We thank the reviewer for carefully reading the manuscript. We agree that the suggested discussion will improve the quality of the manuscript.

R1C2:

The study reveals that spatial differences (total column) between MOZART-4 and IASI are generally largest during local autumn/winter season, with an overestimation compared to IASI observations. This overestimation is most pronounced for IGP South Asia (20°N-32°N, 70°E-95°E), while rather an underestimation is found for NCP East Asia (30°N-40°N, 110°E-120°E), especially during the summer months. On the other hand, the comparison of surface concentrations reveals that the model underestimates the ammonia observations over South and East Asia throughout the year. This is shown by monthly mean (time series) and annual averages (scatter plot), and these results are in contrast to the total column case (model burden w.r.t. IASI observations).

> Yes, we agree with the reviewer's observations that the difference between is most pronounced for IGP South Asia. The following Fig. 1 below shows the time-height distribution of NH_3 and mean planetary boundary layer height (PBLH) averaged over the IGP region, respectively. It can be seen that during winter months, higher

atmospheric stability prevents the mixing of boundary layer NH_3 to the free troposphere over IGP, which is reflected in the higher winter-time values of MOZART-4 NH_3 columns. Similarly, a higher NH_3/NH_4^+ ratio (Fig. S3 in the revised Supplement) and lower dry and wet deposition (Fig. S4 and S5 in the revised Supplement) of NH_3 over IGP in winter months enhances the accumulation of NH_3 in the boundary layer compared to summer months. On the other hand, very little NH_3 gets detected by the satellite at the higher altitudes, where the satellite's detection sensitivity is more than that at the surface (Clarisse et al., 2010). IASI measurements' limited sensitivity to detect boundary layer NH_3 (Van Damme et al., 2014) could be one of the reasons for large differences between MOZART-4 and IASI in winter seasons. Also, the wheat crop sowing over IGP involves a higher fertilizer application rate during peak winter months that releases a significant quantity of NH_3 into the atmosphere. However, this seasonality is largely missing in the emissions (Fig. 2 (top, left in the revised manuscript)), indicating that the winter-time meteorology largely drives higher MOZART-4 NH_3 over this region.

Also, the emission fluxes of SO_2 and NO_x over IGP are only one-fourth of that over NCP (Wang et al., 2020). Therefore, relatively low SO_2 and NO_x concentration could be an important factor for Higher NH_3 columns over IGP during winter.

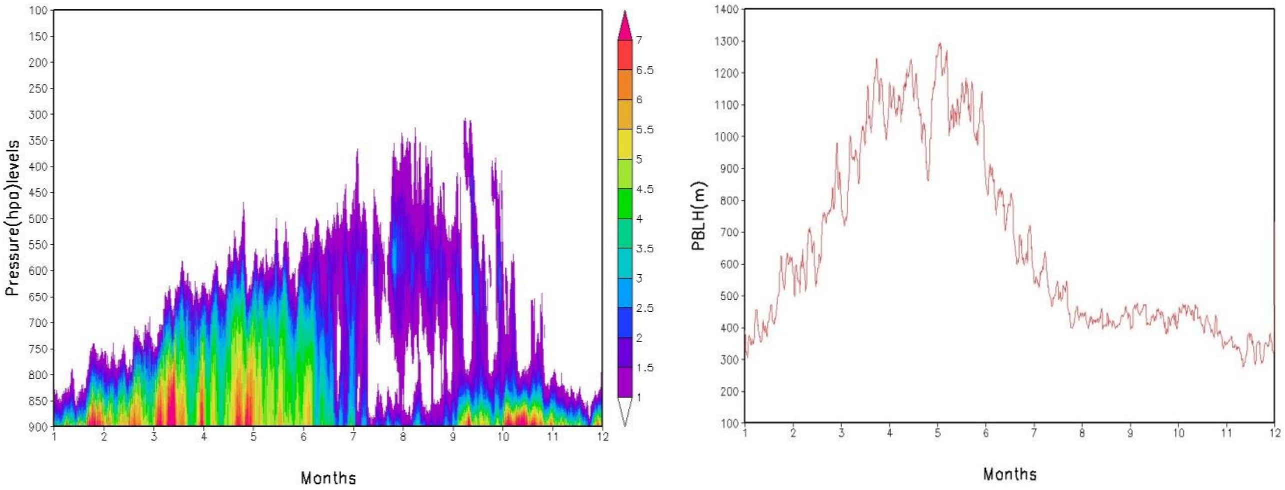

Figure 1: Daily vertical distribution of distribution of NH_3 (ppb) averaged over IGP South Asia (20°N-32°N, 70°E-95°E) (left) and daily mean Planetary Boundary Layer height (PBLH in meters) averaged over IGP South Asia (20°N-32°N, 70°E-95°E) (right)

Despite some potential calibration issue w.r.t. certain observations, there seems to be no obvious inconsistency with the NH_3 observations used in this study. Instead, both issues (model vs surface and total column observations) rather point to an incomplete model set-up w.r.t. the gas-aerosol partitioning assumptions. Nevertheless, I also recommend

that the authors make sure that the study is based on (or includes) quality controlled surface observations.

The quality control and assurance method followed by CPCB for these air quality monitoring stations is given at CPCB (2011 and 2020). The calibration procedures for the NH_3 analyzer conforms to USEPA (the United States Environmental Protection Agency) methodologies and include daily calibration checks, biweekly precision checks, and linearity checks every six weeks. All analyzers undergo full calibration every six weeks. For detail on calibration procedure, refer to CPCB (2020); Technical Specifications for Continuous Real Time Ambient Air Quality Monitoring Analysers (2016). Furthermore, we take the following steps to reassure the quality of NH_3 observations from the CPCB network stations. For data quality, we rejected all the observation values below 1 µg m^{-3} and above 250 µg m^{-3} at a given site if other sites in the network do not show values outside this range. This step aims to eliminate any short-term local influence that cannot be captured in the models and retain the regional-scale variability. Second, we removed single peaks characterized by a change of more than 100 µg m^{-3} in just one hour for all the data in CPCB monitoring stations. This step filters random fluctuations in the observations. Third, we removed some very high NH_3 values that appeared in the time series right after the missing values. For any given day, we removed the sites from the consideration that either experience instrument malfunction and/or appear to be very heavily influenced by strong local sources. This information is updated in the revised manuscript.

In order to verify the data quality of the CBCB monitoring site, we have inter compared the NH_3 measurement at CPCB monitoring station (R.K. Puram) in Delhi with the NH_3 measurements at Indira Gandhi International (IGI) Airport taken during the Winter Fog Experiment (WiFEX) (Ghude et al., 2017) using MARGA (Measurement of Aerosols and Gases) instrument during the winter season of 2017-2018. More details on the NH_3 measurements using MARGA is available with Acharja et al. (2020). Both sites were situated in the same area of Delhi (less than 1km). Our inter-comparison shows that NH_3 measured at CPCB monitoring station by chemiluminescence method are slightly (on an average 9.8 µg m^{-3}) on the higher side than NH_3 measured by ion chromatography (IC) using MARGA (Fig. 2 below). The observed differences could partly be related to the different NH_3 measurement techniques and partly to the locations of the two monitoring sites that were not place exactly at the same location. Apparently, the difference of 9.8 µg m^{-3} indicates that the NH_3 measurements from the CPCB do not suffer from the calibration issue. However, rigorous validation is required in the future with more data sets.

In the revised manuscript we have now included above discussion.

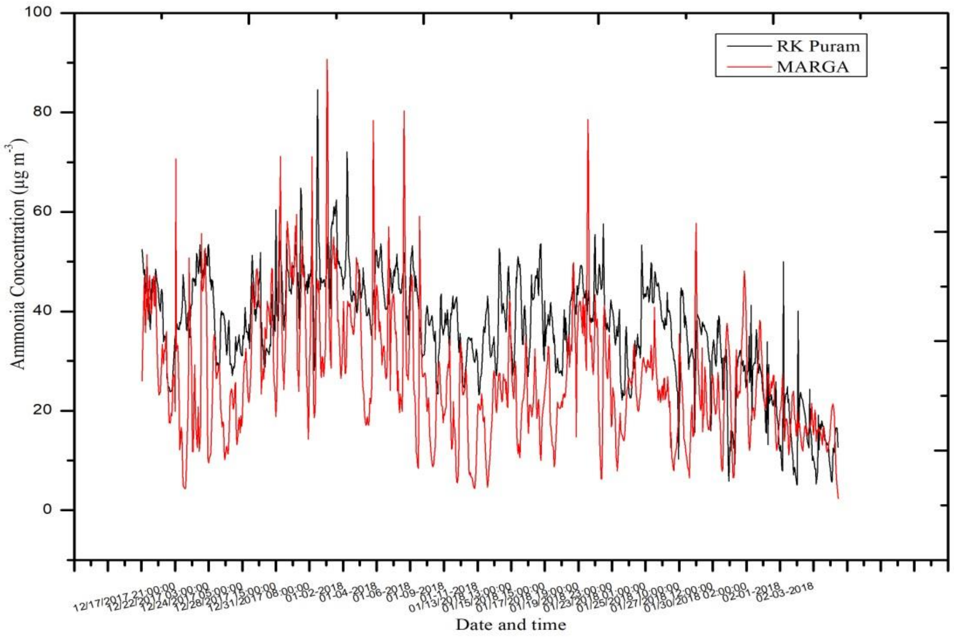

Figure 2. Comparison of NH_3 ($\mu g\ m^{-3}$) concentration from MARGA instrument with RK Puram (CPCB) station

R1C3:

Regarding the modeling assumptions, it should be noted that the chosen set-up has its limitations w.r.t. the NH_3/NH_4^+ partitioning. The main issue here is that in the current set-up, both (i) cations other than NH_4^+, e.g., sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), have been neglected, as well as (ii) organic acids were omitted for the gas-aerosol partitioning calculations. Both are, however, important for the NH_3/NH_4^+ partitioning w.r.t. to real world observations. Nevertheless, since mineral cations and organic acids have been neglected in conjunction, the presented model results could be in terms of yearly averages more or less "right" for the wrong reason, as indicated by a study published sometimes ago in ACP 2006 (https://acp.copernicus.org/articles/6/2549/2006/). On shorter time scales, however, the incomplete model set-up could be a cause of the observed discrepancies.

> Yes, we agree with the reviewer's comment that the current modeling setup has limitations w.r.t. NH_3/NH_4^+. In this present work, the ammonium nitrate distribution is determined from NH_3 emissions based on the parameterization of

gas/aerosol partitioning by Metzger et al. (2002), which is a set of approximations to the equilibrium constant calculation (Seinfeld et al., 1998), based on the level of sulfate present. The application of any equilibrium models (EQMs) in global atmospheric studies is associated with considerable uncertainties. We followed, equilibrium simplified aerosol model (EQSAM)- gas-aerosol partitioning calculations by Metzger et al. (2002) the current setup. The assumptions used in this study are limited to the ammonium-sulfate-nitrate-water system, which is valid for only inorganic salt compounds. This latter was updated (EQSAM2) to account for ammonium-sulfate-nitrate-sodium-chloride-water system, mineral citation, and organic acids (Metzger et al., 2006). Metzger et al. (2006) found that the total ammonium partitioning calculated by updated-EQSAM2 parameterization was 15 % lower than that calculated from the parameterization similar to Metzger et al., (2002). Ammonia has a stronger affinity towards the neutralization of sulphuric acid (H_2SO_4) than nitric acid (HNO_3), whereas the formation of ammonium chloride (NH4Cl(s) or (aq)) in the atmosphere is unstable and can dissociate reversibly to NH_3 and HCL. These aerosols in both dry and aqueous phase evaporate faster than the corresponding ammonium nitrate (NH_4NO_3) aerosols (Seinfeld and Pandis, 2012).

We agree with the reviewer's comment that neglecting sodium-chloride organic acids and mineral cations in the parameterization of gas/aerosol partitioning system in the present work may cause some observed discrepancies. Overall consideration of major mineral cations could lead to more free ammonia, which will potentially increase NH_3 total columns. This will further increase differences (total column) between MOZART-4 and IASI over IGP and a decrease in differences (total column) between MOZART-4 and IASI over NCP. However, the influence of mineral cations on the NH_3 gas–particle partitioning might be limited (Acharja et al., 2020; Dao et al., 2014) and requires further focused studies over south Asia. Discussion is added in the revised manuscript.

R1C4:

The reason is that in this model set-up, the NH_3/NH_4^+ partitioning is mainly controlled by sulfate and subsequently by nitrate, which might be in reality not the case in Asia. Consideration of at least the major mineral cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) might be necessary, since all of them are ubiquitous and preferentially neutralize sulfate, which directly affects the NH_3/NH_4^+ partitioning. In contrast to the semi-volatile compound ammonium nitrate (NH_4NO_3), mineral cations form more stable compounds that exhibit a distinct different temperature dependent dissociation and water uptake, but no volatilization, as it is here the case only for NH_4NO_3. Thus, consideration of additional (mineral) cations could lead to more free ammonia (w.r.t. sulfate neutralization), which, in addition could lead to a larger fraction of ammonia being neutralized by nitric acid (e.g. resulting from lightning and thus adding up in the vertical model column as ammonium nitrate). And, since NH_4NO_3 is unstable at higher temperatures and low

humidities, both cases could result in higher simulated NH_3 concentrations during the summer months resulting in potentially closer NH_3 total column concentrations w.r.t. IASI observations.

> Yes, we agree with the reviewer's comment that in our modeling system, the NH_3/NH_4^+ partitioning is mainly controlled by sulfate and subsequently by nitrate since major mineral cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) are not included. We would like to draw attention to one of our recent study (Acharja et al., 2020) based on analysis of water-soluble inorganic chemical ions of PM_1, $PM_{2.5}$, and atmospheric trace gases over Indo-Gangetic plain (IGP), South Asia, which were monitored by Monitoring AeRosol and Gases in Ambient Air (MARGA). The study revealed that NH_4^+ was one of the dominant ions, collectively with Cl^-, NO_3^- and SO_4^- constituted more than 95 % of the measured ionic mass in both PM_1 and $PM_{2.5}$. The remaining ionic species (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) formed constituted only about 3 % of the total measured ions. Although major mineral cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) contribute actively in a neutralization reaction, but their concentration in IGP was found to be very low. Whereas over NCP, NO_3^- and SO_4^- were found to be dominant ions followed by NH_4^+ and Cl^- which collectively contributed more than 86-90 % in both PM_1 and $PM_{2.5}$. Other mineral cations contributed less than 5 % in PM_1 and $PM_{2.5}$ (Dao et al., 2014). Furthermore, in one of the studies, over East Asia, the neutralization capacities of major cations (e.g., K^+, Ca^{2+}, Mg^{2+} and NH_4^+) were individually estimated by estimating the Neutralization Factors (NFs) for interpretations. It was found that NH_4^+ was the predominant neutralizing cation with the highest NF (above 1), whereas K^+, Ca^{2+} and Mg^{2+} contributed relatively low in the neutralization of aerosol acidity with the lowest NF (below 0.2) (Xu et al., 2017). Hence, consideration of mineral cations may contribute in minor in the neutralization of acidic aerosol over Asian region; still, a rigorous study is needed in future. Therefore, consideration of mineral cations and organic acids on the NH_3/NH_4^+ partitioning might be limited and will not significantly impact the results of this study.

R1C5:

Also, the underestimation of the surface NH_3 concentrations throughout the year over both South and East Asia could be a result of missing mineral cations in this model set-up. In reality, a larger fraction of sulphate might be neutralized by mineral cations rather than just by ammonium, which could lead to a larger fraction of free ammonia near the surface. Also, since both nitrates and sulfates preferentially react with mineral cations, nitric acid (e.g. from the traffic sector) might be neutralized by ammonia in a lower amount in reality, as it seems to be the case in this model set-up. In any case, consideration of mineral cations could also lead to a larger fraction of free ammonia near the surface, which might be even sufficient to explain discrepancies with surface observations.

> Metzger et al. (2006) results have shown that only if (soluble) mineral components and (lumped) organic acids are accounted for, the observed gas-aerosol partitioning of

ammonia and nitric acid can be accurately reproduced for air pollution episodes. Hence, while comparing model results with surface observations, incorporating mineral cations may lead to an increase in free ammonia near the surface, but change will not be significant (considering a 15 % increase) (Metzger et al., 2006). We have added the above description in the discussion section for explaining discrepancies with surface observations in the revised manuscript.

R1C6:

Furthermore, due to the excess of ammonia in this model set-up, ammonium nitrate can be formed in both regions, although the simulated sulfate concentrations (burden) are higher in East Asia compared to South Asia. And, due to its semi-volatile character, the seasonal variability of NH4NO3 and the associated NH3 concentrations differ in both regions as observed. Since NH4NO3 is unstable at higher temperatures, more NH3 bound as NH4NO3 (compared to ammonium sulfate) can lead to higher NH3 concentrations during summer, as it is observed in East Asia. In South Asia, where both ammonia and sulfate concentrations are lower, also NH4NO3 concentrations are lower and thus the seasonality of NH3 is less pronounced, which is consistent with the surface observations.. In South Asia, where both ammonia and sulfate concentrations are lower, also NH_4NO_3 concentrations are lower and thus the seasonality of NH_3 is less pronounced, which is consistent with the surface observations.

Yes, we agree with reviewer.

We have added this information in the revised manuscript. We agree with the reviewer, the seasonal variability of NH_4NO_3 is strong during summer over East Asia as shown in the below Fig. 3 (Fig. S6 in the revised Supplement), which can lead to higher NH_3 concentrations during summer over East Asia.

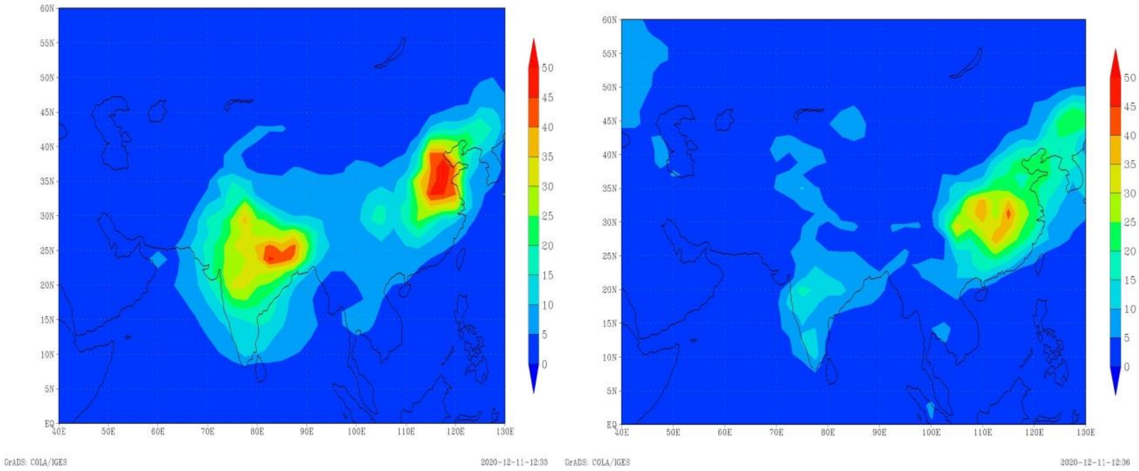

Figure 3. MOZART-4 model estimate of NH_3NO_3 wet deposition flux ($\times 10^{-9}$ kg m^{-2} s^{-1}) during summer (JJA) season (left) and during winter (DJF) season (right)

R1C7:

On the other hand, the overestimation of the IASI total column NH_3 concentrations over South Asia, for most of the year except the summer months, could be also a result of missing anions, e.g., of organic acids, assuming the vertical exchange processes are more or less realistically modelled. However, considering mineral cations without additional acids, could likely cause even larger differences in this case (for details see e.g., https://acp.copernicus.org/articles/6/2549/2006/).

Yes, we agree with the reviewer's comment that the current modeling setup has a limitation with respect to mission anions of organic acids and could be one of the regions between observed and model discrepancies. We want to bring to reviewers' notice that model NH_3 total column concentrations are larger than IASI total column over South Asia (Fig. 4 in the revised manuscript) during most of the years, except during summer months where IASI total columns are larger than the model (Fig. 8 in the revised manuscript). It can be seen in above Fig. 1 (reply to R1C2) that during winter month's higher atmospheric stability prevents the mixing of boundary layer NH_3 to the free troposphere over IGP, which is reflected in the higher wintertime values of MOZART-4 NH_3 columns. Similarly, higher NH_3/NH_4^+ ratio and lower dry and wet deposition of NH_3 over IGP in winter month enhances the accumulation of NH_3 in the boundary layer compared Limited sensitivity of IASI measurements to detect boundary layer NH_3 (Van Damme et al., 2014) could be one of the reasons for large differences between MOZART-4 and IASI in winter seasons. On the other hand, heating of the landmass due to large solar incidence suppresses the wintertime subsidence over the IGP and leads to a deeper boundary layer during spring and early summer (the average PBLH is about 1100 m, 600 m deeper during spring and summer compared to winter over IGP). During this season, significant transport of the boundary pollution in the mid and upper troposphere due to enhanced convective activities and large scale vertical motion can be noticed. Vertical motion associated with the convective activities is expected to redistribute the NH_3 concentration in the column, leading to more NH_3 at the higher altitudes where the satellite's detection sensitivity is more than that of the surface (Clarisse et al., 2010). As a result, more NH_3 gets detected by the satellite, and we see less difference between observations and model over the IGP.

Therefore, the addition of missing anions will further cause a larger difference between Model and IASI total column NH_3 concentrations over South Asia during most of the months, except during summer where the difference between Model and IASI total NH_3 column will decrease.

R1C8:

Unfortunately, these processes (briefly touched on above) are missing in most modelling studies, and I fear their consideration is also beyond the scope (or possibilities) of this study?

We thank the reviewer for putting this additional information to improve the understanding of NH_3/NH_4^+ gas-aerosol partitioning. Yes, since we followed parameterization of gas/aerosol partitioning by Metzger et al. (2002), unfortunately, additional mineral cations and organic acids are missing in our modeling study, which is important in gas-aerosol partitioning of reactive nitrogen. For accurate reproducing modeling results and real comparison to observations, EQMs play an important role in determining NH_3/NH_4^+ gas-aerosol partitioning.

As mentioned previously, over Asia, chemical characterization of water-soluble inorganic chemical ions of PM_1, $PM_{2.5}$ and atmospheric trace gases reveals that major mineral cations' concentration is very low in PM_1 and $PM_{2.5}$. Lack of study on the presence of organic acids over Asia limits our understanding. Hence, due to a poor understanding of the impact of organic species on aerosol (Zaveri et al., 2008), organic species are not considered in the thermodynamic calculations. However, EQMs are associated with considerable uncertainties and assumptions. According to Metzger et al. (2006), the total NH_3/NH_4^+ gas-aerosol partitioning calculated ammonium-sulfate-nitrate-sodium-chloride-water system was about 15 % lower than that calculated by EQSAM2 (Equilibrium Simplified Aerosol Model) considering organic acids, and the above study was based upon Greece, which might not be the similar case for the Asian region. Thus, to study the influence of mineral cations and organic species on the NH_3 gas-particle partitioning need rigorous study over the Asian region. Currently, this new setup will be out of our scope. However, in future work, we will try to use EQSAM2 to study the effect of additional mineral cations and organic acids on ammonium gas-aerosol partitioning.

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