Response to Anonymous Referee #1's Comments

First of all we thank the reviewer for the positive evaluation of 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 of anonymous referee #1. These comments are indicated in **bold**, whereas the author's response is presented in blue.

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 readability 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).

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 Central Pollution Control Board (2020). 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 observations 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. The purpose of this step is to eliminate any short-term local influence that cannot be captured in the models and to retain the regional-scale variability. Second, we removed single peaks that are 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.

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.

- In this present work, the ammonium nitrate distribution is determined from NH_3 emissions and 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 sulphate present. We followed, equilibrium simplified aerosol model (EQSAM)-Metzger et al. (2002) gas-aerosol partitioning calculations. 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 which additionally accounted for organic acids (Metzger et al., 2006). The application of any equilibrium models (EQMs) in global atmospheric studies is associated with considerable uncertainties. Metzger et al. (2006) found that the total ammonium calculated by ammonium-sulfate-nitrate-sodium-chloride-water system was about 15 % lower than that calculated by Equilibrium Simplified Aerosol Model 2 (EQSAM2) which includes additional organic acids. Ammonia has stronger affinity towards neutralization of sulphuric acid (H_2SO_4) than nitric acid (HNO_3) whereas formation of ammonium chloride ($NH_4Cl_{(s)\ or\ (aq)}$) in atmosphere is unstable and can dissociate reversibly to NH_3 and HCL. This aerosols in both dry and aqueous phase evaporate faster than the corresponding ammonium nitrate (NH_4NO_3) aerosols (Seinfeld and Pandis, 2012). Thus, the influence of mineral cations and organic species (scarce study over Asia) on the NH_3 gas–particle partitioning might be limited and will not have a large significant impact on the results of this study if we consider 15 % uncertainty. Hence, we agree with the reviewer neglecting mineral cations and organic acids may cause observed discrepancies in a minor way. 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.

- 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 $PM_{2.5}$. Remaining ionic species (i.e., 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 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 both PM_1 and $PM_{2.5}$ (Dao et al., 2014). Furthermore, in one of the study, over East Asia, the neutralization capacities of major cations (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 neutralization of aerosol acidity with lowest NF (below 0.2) (Xu et al., 2017). Hence, consideration of mineral cations may contribute in minor in neutralization of acidic aerosol over Asian region, still rigorous study is needed in future.

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, incorporation of mineral cations may lead to increase in free ammonia near surface but change will be not be significant (considering 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 NH_4NO_3 and the associated NH_3 concentrations differ in both regions as observed. Since NH_4NO_3 is unstable at higher temperatures, more NH_3 bound as NH_4NO_3 (compared to ammonium sulfate) can lead to higher NH_3 concentrations during summer, as it is observed in East Asia. 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 revised manuscript in the discussion section of 3.3 to explain seasonal discrepancies with surface observations over both South and East Asia. 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. 1 (figure S2 in the revised supplement), which can lead to higher NH_3 concentrations during summer over East Asia.

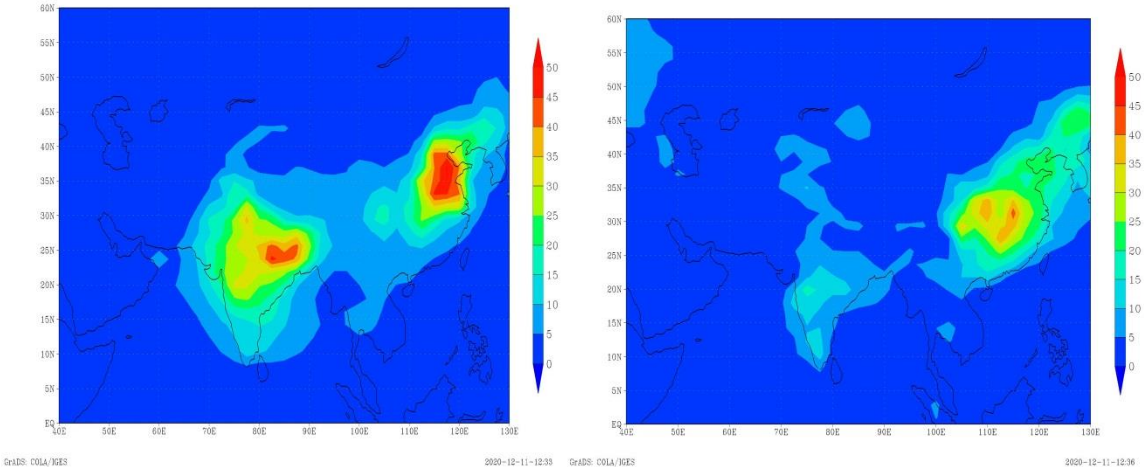

Figure 1. MOZART-4 model estimate of NH_3NO_3 wet deposition flux ($\times10^{-9}$ kg m^{-2} s^{-1}) during summer (JJA) season (left) and during winter (DJF) season (right)

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 only if the additional anions from (lumped) organic acids are taken into account in the EQSAM2 model, ammonium realistically partitions into the aerosol phase. This resulted the predicted average ammonium partitioning is comparable to the observations within 1–2% for both the aerosol fine and coarse mode (Metzger et al., 2006). As explained previously, we agree with the reviewer for accurate comparison, absence of major cations and organic acids (currently, study of field measurements of organic acids in Asia is least done) in this current set up may explain the overestimation of modeled NH_3 total columns for most of the year except summer months over South Asia.
- Explanation is added in revised manuscript in section 3.3.

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 you 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 are important in gas-aerosol partitioning of reactive nitrogen. For accurate reproducing modeling results and real comparison to observations, EQMs play important role in determining NH_3/NH_4^+gas-aerosol partitioning.
- But as mentioned previously, over Asia, chemical characterisation of water soluble inorganic chemical ions of PM_1, $PM_{2.5}$ and atmospheric trace gases reveals that concentration of major mineral cations is very low both in PM_1 and $PM_{2.5}$. Due to lack of study on the presence of organic acids over Asia limits our understanding. Hence, due to poor understanding of 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) total ammonium NH_4^+ 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 Asian region. Thus, to study the influence of mineral cations and organic species on the NH_3 gas–particle partitioning need rigorous study over Asian region. Currently this new setup will be out of our scope, but 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.

References

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