Interactive comment on "Analysis of atmospheric ammonia over South and East Asia based on the MOZART-4 model and its comparison with satellite and surface observations" by P. Pawar et al.

Anonymous Referee

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.

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.

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 some times 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.

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.

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 sulfate 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.

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.

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/).

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?