Responses to Comments by Reviewer 2

Based on an extensive ship-based observations of aerosol NO3 and NH4 concentrations in globe, this manuscript assesses the performance of simulated N concentration and deposition fluxes over three remote oceans. This is a very impressive manuscript that reports on the model-observation comparisons and is generally well written. This manuscript is thus a significant contribution to understanding state-of-the-art model limitations for annual average, seasonality, and spatial patterns. The primary shortcomings in the manuscript include: clarification of the methodology of models used, uncertainties due to emissions and meteorological forcing data, sensitivity of the model-observation comparisons on the size of spatial window, rationality of model-observation comparison analysis on deposition fluxes, implications for atmospheric community in improving models. I presented the review of the paper into separate main topics corresponding to different section of the manuscript.

Response: We thank the reviewer for their thoughtful and constructive comments on our manuscript. We set out our responses (blue text) to these in detail below, together with proposed changed to the manuscript (indented text).

Abstract: The first paragraph should be shortened as much as possible to indicate the importance of model-observation comparisons as well as the influence of mineral dust on N depositions.

Response: We have shortened this paragraph as much as possible, while adding the information on the influence of mineral dust requested by the reviewer.

> Anthropogenic nitrogen (N) emissions to the atmosphere have increased significantly the deposition of nitrate (NO_3^-) and ammonium (NH_4^+) to the surface waters of the open ocean, with potential impacts on marine productivity and the global carbon cycle. Global-scale understanding of the impacts of N deposition to the oceans is reliant on our ability to produce and validate models of nitrogen emission, atmospheric chemistry, transport and deposition. In this work, ~2900 observations of aerosol NO_3^- and NH_4^+ concentrations, acquired from sampling aboard ships in the period 1995 - 2012, are used to assess the performance of modelled N concentration and deposition fields over the remote ocean. Three ocean regions (the eastern tropical North Atlantic, the northern Indian Ocean and northwest Pacific) were selected, in which the density and distribution of observational data were considered sufficient to provide effective comparison to model products. All of these study regions are affected by transport and deposition of mineral dust, which alters the deposition of N, due to uptake of nitrogen oxides (NO_x) on mineral surfaces.

The methodology in the second paragraph is much hard to follow: why choose TM4? How about the two commonly applied methods to calculate N deposition fluxes for CalDep? Does CalDep have the results of deposition fluxes of NOy and NHx? Are NOy and NHx derived from wet and dry depositions? Is it possible to compare nitrate and ammonium with ACCMIP means? In addition, is it possible to separate the contributions of deposition velocities and N concentration to model-observation discrepancy? I believe that it is much importance for scientific community to improve the model-related works in the future.

Response: We have completely rewritten this paragraph, in response to comments by both reviewers (see response to Reviewer 1).

Introduction: Line 71-73: A few of global atmos. Models has been applied for large scale assessment of N deposition over oceans, such as Dentener et al. (2006), Wang et al. (2015), etc. such works should be cited: Dentener, F., Drevet, J., Lamarque, J. F., Bey, I., Eickhout, B., & Fiore, A. M., et al. (2006). Nitrogen and sulfur deposition on regional and global scales: a multimodel evaluation. Global Biogeochemical Cycles, 20(4), 16615-16615; Wang, R., Balkanski, Y., Bopp, L., Aumont, O., Boucher, O., & Ciais, P., et al. (2015). Influence of anthropogenic aerosol deposition on the relationship between oceanic productivity and warming. Geophysical Research Letters, 42(24), 10745-10754.

Response: We have added some citations of modelling studies of N deposition to the ocean, as the reviewer suggests.

Lin 88-89: again, please explain why choose TM4 in this study

Response: We chose to incorporate results from TM4 into the study because the model has a comprehensive atmospheric N cycle description, including Fe redox reactions and organic nitrogen (Kanakidou et al., 2012; Kanakidou et al., 2016) and it allowed us access to parameters associated with particulate NO_3^- and NH_4^+, which were not available from ACCMIP.

> Therefore, in the present study, TM4 speciated results are more appropriate for comparison to the observations and are put in context when used jointly with the more robust, but less speciated, ensemble model results of ACCMIP.

Lin 105-108: Sampling biases due to multiple sources should be discussed in details. Is any type of samples excluded based on sampling regulation related to N deposition in this study? It is better to describe the sampling regulation (sampler, period, temporal resolution, size fractions, sampling method, analytical method, etc) in main text or SI file or the dataset SOLAS

Response: We have added further information on the methodologies for the source observations to Table S1 in the Supplementary Material and added more text to the main manuscript to explain the rationale for selecting data to include in the database.

> Since the data originate from multiple sources, the samples were acquired using a variety of sampling devices (e.g. bulk filtration or in size fractions using cascade impactors), collection substrates (e.g. Whatman 41, glass fibre or quartz) and sampling intervals and were analysed using different techniques (commonly ion chromatography or automated spectrophotometry) in many different laboratories. (A summary of the available information on sample collection procedures is given in Table S1). Standard procedures for aerosol inorganic N sampling and analysis have not yet been established, and nor have inter-laboratory intercomparison / intercalibration exercises (e.g. Morton et al., 2013) been commonly held. In the absence of such procedures, datasets were accepted into the database that had either already been published in the peer-reviewed literature or that originated from laboratories with established publication records. Under these conditions, the presence of biases within the observational database cannot be ruled out. Sampling intervals varied between 12 and 48 hours, but the majority of samples were collected over ~24 hours.

Methods: Line 127: Explain the abbreviation ECMWF first, and justify why choose ECMWF. Actually a few of reanalysis datasets including surface wind speed could be used for estimating Vd. Could you please discuss more on the uncertainties due to the choice of meteorology dataset?

Response: We have added “European Centre for Medium-Range Weather Forecasts” for ECMWF and included a discussion of the uncertainties introduced through the choice of meteorology (see responses to Reviewer 1).

Line 128: what is the difference between variable Vd model and well-tested deposition velocity model in previous works? How to calculate aerodynamic resistance and quasi laminar boundary layer resistance? A detail of variable Vd model should be provided in SI file.

Response: We think the reviewer has concluded that we developed a new model for Vd, but we in fact used the well-established model of Ganzeveld et al. (1998). We have altered the text describing our use of this Vd model to explain this more clearly.

> Dry deposition fluxes were also calculated using wind speed-dependent values of v_d for particles of 7 µm (coarse mode) and 0.6 µm (fine mode) diameter using the parameterisation of Ganzeveld et al. (1998). This “variable v_d” method is similar to the approach used previously to estimate dry deposition of N species to the Atlantic Ocean by Baker et al. (2010) and Powell et al. (2015). In this case, European Centre for Medium-Range Weather Forecasts (ECMWF) ERA Interim reanalysis dataset surface wind speeds were obtained for the years 1995 – 2012 and the mean wind speed for these years was used to calculate v_d for each grid cell.

2.3 model products: I strongly suggest introducing the methodology of TM4 model in SI file, forcing data, emissions of N, simulation setup, etc

Response: The information requested by the reviewer is covered in detail in Kanakidou et al. (2016) and references therein. There is no need to repeat that information in the SI.

Line 139: how to compare modeled N deposition at coarse scale with site-scale observations?

Response: This is a perennial problem for model – observation comparisons. The underlying assumption in all such cases is that the available observations are representative of the model grid scale, which is a plausible assumption for the open ocean. The manuscript contains considerable discussion of the validity of that assumption for the present study.

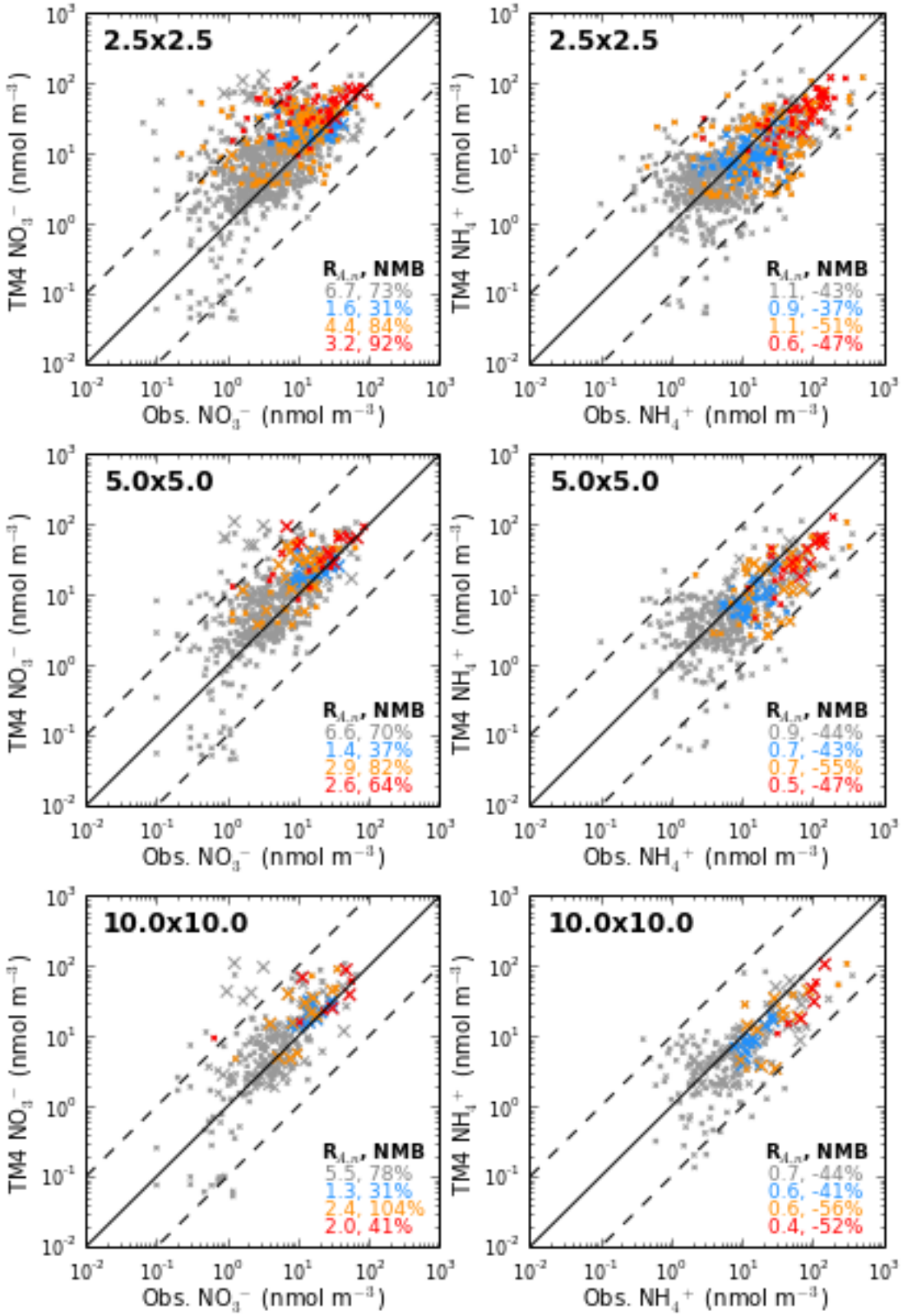
Line 152-153: CalDep is based on the observations for the period of 1995 to 2012, but ModelDep is simulated for a specific year (2005 for TM4, 2000 for ACCMIP MMM).

Response: Yes, that is correct. Had sufficient observations been available for us to focus the comparison on the model simulation periods, we would have done so. Unfortunately remote ocean observations of aerosol composition are not so abundant.

Line 172: Spatial window of 5ËŽ 5ËŽ is used for model-observation comparisons. Could you please check whether the result is independent of the size of spatial windows?

Response: In order to illustrate the impact of grid scale on the comparisons we make in the manuscript, we have repeated the observation – model comparisons for aerosol nitrate and ammonium concentrations at three different resolutions (2.5°x2.5°, 5°x5° and 10°x10°). The results of that analysis are shown below (note that, in order to examine the 10°x10° resolution, the boundaries of the study regions were expanded to 0, 40, -40, -10 (NEAtl), -10, 30, 50, 90 (NInd) and 10, 40, 110, 140 (NWPac) (all °S, °N, °W, °E). While there were some differences in values of $R_{A,n}$ and

NMB between resolutions, these did not impact the conclusions of the study and we therefore consider that our results are robust to changes in grid resolution.



Results and Discussion Line 203: explain the abbreviations TEAtl, NInd and NWPac. I suggest to use the full name of study regions in main text, but abbreviations in Tables or Figures.

Response: The abbreviations TEAtl, NInd and NWPac were defined at the end of Section 1 (lines 94-95 of the Discussion manuscript). We prefer to leave the use of these abbreviations as they were.

Line 333: I am not sure if it is necessary to have subtitles in the main text according to ACP style.

Response: The use of subtitles is consistent with ACP style. We have left these as they were, because we feel that they aid the reader.

Line 340-349: the total columns of NH3 retrieved from IASI satellite observations would be an effective way to validate the spatio-temporal patterns of ammonia, referring to: Van Damme, M.; Clarisse, L.; Heald, C. L.; Hurtmans, D.; Ngadi, Y.; Clerbaux, C.; Dolman, A. J.; Erisman, J. W.; Coheur, P. F. Global distributions, time series and error characterization of atmospheric ammonia (NH3) from IASI satellite observations. Atmos. Chem. Phys. 2014, 14 (6), 2905–2922.

Response: We appreciate the reviewer's suggestion, but we do not feel that total column gas-phase ammonia satellite retrievals are likely to prove effective in helping to constrain the exclusively surface-level processes considered in our manuscript.

Line 350-353: Besides of the effect of pH, the inconsistency of sampling regulation for ship-based observation would be another source of biases. Please discuss in details on it.

Response: We already discussed the likely bias introduced through losses on cascade impactor samplers (lines 334-339 of Discussion document). Although the text highlighted by the reviewer focuses on effects driven by pH, the impacts of those effects vary primarily according to sampling methodology (e.g. whether, or not, aerosol particulates are size-segregated at the point of collection). We have added text to emphasise this.

> Thus, there are a variety of processes, particularly in the marine environment, that can lead to positive and negative biases in measured aerosol NO_3^- and NH_4^+ concentrations, and the extent to which a given dataset is affected by these processes is greatly influenced by sampling methodology. If such effects have influenced the database used here, biases are unlikely to be uniform across all the observations, since the observations come from a very wide variety of sources with many different sample collection protocols (see Table S1).

Subsection 4.2: Model-observation comparisons should focus on the difference in aerosol concentrations, but not on that in deposition fluxes. Actually CalDep deposition fluxes are also derived based on two simple methods, where the uncertainty of dry deposition velocity cannot be rationally quantified in this study.

Response: We agree with the reviewer. The lack of species concentrations reported in the ACCMIP product forces us to use a deposition comparison in this case. The concentration comparisons we report for TM4 are clearly preferable, but the inclusion of deposition comparisons for TM4 allows us to draw parallels with the less than optimal evaluation of ACCMIP that we have been forced to make. We have amended the Abstract to emphasise this point (see response to Reviewer 1).

Subsection 4.3: I guess that the discrepancy in seasonality between modeled and observed N depositions would be due to the uncertainties of emission source and meteorological data. It would be of use to discuss in details on their influences.

Response: We have added additional text to discuss the potential influences on seasonality in N deposition in the northern Indian Ocean region.

> Differences in N deposition seasonality between models and observations in this region might arise as a result of a number of factors. These include: seasonal variations in N emissions used in the models (see for instance discussion in Daskalakis et al. (2015) for seasonal and spatial differences in biomass burning emission databases, Figs. 1 and S2 of that paper), biases in seasonal variations in meteorology (e.g. in precipitation rates (Srinivas and Sarin, 2013) and wind fields), and seasonal changes in mineral dust composition, in particular calcium content, over the region (Srinivas and Sarin, 2013) affecting the uptake of NO_x onto dust particles.

Subsection 4.4: please extend the discussion on the role of mineral dust on N deposition. It would be better to specify the limitation of models, such as TM4 and ACCMIP multi-model ensemble?

Response: See our response to the comments by Reviewer 1 on this issue.

Conclusions: it is too long to follow as conclusion of the manuscript. I suggest to shorten it and focus on the main findings on the limitation of current models in estimating particulate N depositions and the recommendations on improving the models for atmospheric modeling community.

Response: We altered the text in this section (now titled "Summary and Conclusions", as suggested by Reviewer 1) in order to address the comments of both reviewers. (See response to Reviewer 1).

References

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