

Response to Reviewer 1

We thank the reviewer for his/her careful evaluation of the manuscript. We especially appreciate the reviewer's comments providing references to recent work on uptake coefficients and mineralogy information. We think adding discussion on these topics has greatly improved our paper. Below we give a detailed response to each of the concerns raised by the reviewer. Reviewer's comments are in regular font and our replies are in bold font characters.

General comments

This study examines the effects of dust particles on tropospheric chemistry through the inclusion of heterogeneous reactions at the particle surface and the radiative effects on the photolysis rates. Several additions have been made to WRF-Chem to accommodate the new chemical reactions and the responsiveness of the photolysis rates at the presence of atmospheric dust particles. The paper is in line with the current state-of-the-science in the field of atmospheric chemistry. Even though a lot of similar applications have appeared in the literature, the area under investigation in India provides a new element that adds to the scientific knowledge on the aerosol processes in that specific region. The title of the manuscript reflects the content of the paper and is considered sufficient. I am in favor of publishing the paper with Atmospheric Chemistry and Physics, after carefully addressing the specific comments that follow.

Specific comments

The results from this study are highly related to one specific dust event (model simulation for 15 days in April 2010) and cannot be generalized for all dust events in the region. This should be acknowledged in the abstract and summary of the manuscript.

Dust storms in northern India are characterized by large increase in AOD (>50%) and decrease in α (>70%) (Dey et al., 2004; Prasad and Singh, 2007). Both these features were observed during this dust storm indicating that this was a typical pre-monsoon season dust storm (see Kumar et al., 2014 for further details) and can be considered as representative of dust storms in northern India. We already mentioned this dust storm as “typical” in both the abstract and the summary, and this is now acknowledged in section 4.1 also. However, following the reviewer's suggestion, we have added the following line in summary. “Although this study analyzed a typical dust storm in northern India but more such studies should be conducted in future to lend further confidence in these results”.

How are the products from the heterogeneous reactions treated in the model? For example, the sulfates produced on dust are added to the sulfates produced from gas to particle conversion or they are kept separately in the thermodynamics and the other aerosol processes in the model? This is important to understand the results from the simulations.

The gases reacting with dust particles are assumed to be lost irreversibly on the particle surface but do not contribute to aerosol mass in the model configuration used here. This is

because we use the GOCART aerosol module, which does not include an aerosol thermodynamic module in WRF-Chem. We agree that heterogeneous uptake of trace gases by aerosols can potentially affect aerosol mass, composition and size distribution. However, the main objective of this study was to understand the impact of a dust storm on the levels of trace gases only. The GOCART model is suited to meet this objective. We have now included this information in section 2.2.

The discussion of aerosol thermodynamics in WRF-Chem is absent in the manuscript and should be included in the text. The product of the heterogeneous reactions at the surface of dust particles is a new particle, as described in section 2.3 (atmospheric aging). It can be sulphate or nitrate covering the dust particle, after the adsorption of the related gaseous compound. That new particle takes part in all aerosol processes (thermodynamics, deposition, advection etc.)? This should be clearly stated in the text.

As stated in our reply above, the GOCART aerosols scheme does not consider aerosol thermodynamics. In Section 2.3, we discuss the simplified treatment of atmospheric aging of dust aerosols in which aged dust particles are treated similar to the original dust particles and take part in advection and deposition processes but not in aerosol thermodynamics. The limitation of our study due to use of the GOCART model and need for a detailed aerosol module for future studies are already discussed in the second last paragraph of summary.

The publication by Crowley et al. (2010) is dedicated to the heterogeneous processes on surfaces of solid particles present in the atmosphere, for which uptake coefficients and adsorption parameters have been presented at the IUPAC (International Union of Pure and Applied Chemistry) website in 2009 (<http://iupac.pole-ether.fr/>). In this publication, data of uptake coefficients is evaluated and a recommendation is made for each reaction, based on several arguments presented in the paper. A reference to this work must be included in the text, as it is a recent study based on experimental data and it is closely related to this work. A brief discussion on the consequences from using lower or higher values for the gamma coefficients compared to the ones in Table 1 should be included in the text. Sensitivity runs with different gamma coefficients would be a more appropriate way of assessing the uncertainties that are related with the adoption of one value.

We have included this reference in the revised manuscript. We also conducted two sensitivity simulations using lower and upper bounds of γ values reported in the literature. The results from these sensitivity simulations are now discussed in a new section (4.6) called “Effects of uncertainty in reactive uptake coefficient (γ)”.

Another important aspect of the heterogeneous formation on the surface of dust particles is the mineralogy of the dust itself. The chemical composition of dust is essential for the realization of several reactions and for the behavior of the particle in the atmosphere. Especially for the HNO₃ uptake, it is important to know how much CaCO₃ is available as the reaction of HNO₃ with CaCO₃ has a different path than that with the rest of the minerals (Grassian 2002). There is no

discussion on this aspect anywhere in the text and I strongly suggest to devote a part in this discussion. The mineralogy of dust particles is very difficult to measure worldwide and only recently we have some compilation of mineralogy databases from scientists in Europe and the US. These can be informative for assuming a percentage of the dust particle as CaCO₃.

We thank the reviewer for bringing this to our attention. At least, two pathways of HNO₃ reaction on mineral dust particles are observed depending on the mineral with which HNO₃ is reacting (Grassian, 2002). Surface-limited reactions are observed when HNO₃ molecules react with Al₂O₃, Fe₂O₃, or TiO₂, whereas both surface and bulk reactivity are observed for HNO₃ reacting with CaCO₃. The first pathway leads to adsorption of HNO₃ molecules to the surface of dust particles thus making it available for renoxification processes while the second pathway leads to irreversible removal of HNO₃ molecules. Peterson (1968) estimated that dust particles in India contain about 20% of CaCO₃. If we assume that 20% of the total HNO₃ molecules reacting with dust particles are lost irreversibly and that the remaining 80% adsorb to the surface, then the reaction of one HNO₃ molecule with a dust particle should be associated with the production of 0.4 molecules of NO_x. This is assuming a yield of 50% for NO_x production from HNO₃ uptake as observed by Chen et al. (2011). In our simulations, we did not consider these different pathways but assumed that HNO₃ reacting with all minerals adsorbs to the surface, and consequently assumed a production of 0.5 molecules of NO_x from HNO₃ uptake (Dust_JH configuration). However, this assumption should not affect the results presented in this study. The comparison between the NO_x distributions as simulated by Dust_JH and Dust_JH_NoReNO_x, showed that the renoxification process leads to a very small (0.1-0.2 ppbv) increase in NO_x values. The use of a yield of 0.4 molecules of NO_x from HNO₃ uptake should lead to an even smaller increase. We have now included this information in section 2.2.

For the model configuration my comment is on the coarse resolution of the gridded domain. I would expect to see a higher resolution simulation, i.e. 10km or 5km, to capture the fine scale of the chemical reactions. Have the authors tried to use a finer spatial resolution? How did they come up with the specific choice?

The use of a finer resolution will not only affect the scale of chemical reactions but might also have influence on modeled dust emissions because the wind speed might vary somewhat with grid spacing. However, we did not use a finer spatial resolution because the anthropogenic emissions used here (MACCity emission inventory; Granier et al., 2011) are only available at a resolution of 0.5°x0.5°. Emission inventories at higher spatial resolution (e.g. HTAP emission inventory at 0.1°x0.1°) have become available only recently and can be used in future simulations.

I am not in favor of referring to accompany papers for parts of the manuscript that ought to be included in the text. Especially when the accompany paper is still under review. This comment

refers explicitly to the initialization of the WRF model as it relates to the meteorology and thus the dust emissions generated by the model, which are essential part of this work.

The accompanying paper has now been published in ACP. We have also included a more detailed description of the model configuration in the revised Section 2.

Supplement: In some occasions the wording in the supplement is not appropriate: i.e. “Both the methods use the SSA...” should be “Both methods use the SSA...” A careful review of the text is necessary.

We have carefully revised the text in both the manuscript and the supplementary material.

Response to Reviewer 2

We thank the reviewer for his/her careful evaluation of the manuscript. Below we give a detailed response to each of the concerns raised by the reviewer. Reviewer's comments are in regular font and our replies are in bold font characters.

The manuscript by Kumar and co-authors tempted to investigate the impacts of a premonsoon season dust storm event on the regional tropospheric chemistry over India. In order to achieve their goal, they further developed the WRF/Chem model by incorporating a number of heterogeneous chemistry reactions and considering the effects of dust particles on photolysis rates of major gas species. They found by including those model treatments, the discrepancies between model and observations can be reduced. The paper also examined the impacts of various model treatments such as RH on heterogeneous reaction rates and aerosol coating effects. The topic of the work is of scientific interests to the journal and contributes to the scientific understanding of the complex interactions between gases and aerosols in the regional model. However the following comments/suggestions need to be addressed before it can be accepted for publication.

Major comments:

One of my major concerns about the model treatments is the neglect of products of the heterogeneous reactions especially for those are associated with nitrogen and sulfur species. There are many recent studies including laboratory experiments, field measurements, and global/regional modeling studies (e.g., Tang et al., 2004; Fairlie et al., 2010; Li et al., 2010; Manktelow et al. 2010; Li et al., 2012; Wang et al. 2012) that have found the significant impacts of dust associated heterogeneous chemistry on the formation of aerosol nitrate and sulfate especially over Asia (with very high anthropogenic SO₂ and NO_x emissions and frequent dust storms), which in turn can modulate the aerosol thermodynamics. The authors did a few sets of hypothetical simulations assuming the dust particles coated with nitrate and sulfate, however those simulations can be done better by explicitly adding the aerosol products or aerosol precursor gases such as HNO₃ into the model treatment. This limitation needs to be discussed or be addressed through sensitivity simulations.

We agree that heterogeneous chemistry can potentially affect aerosol composition and thermodynamics but the focus of this study was to understand the impact of a dust storm on the levels of trace gases only. The GOCART aerosol model does not have an aerosol thermodynamic module and thus it was not possible to consider the products of heterogeneous reactions in the particle phase in this study. We now include this information in the revised manuscript. The limitations of using the GOCART model and need for a detailed aerosol module for future studies are already discussed in the summary.

Another concern is about the approach to determine the tuning factor C in the dust emission equation. A more conventional way to set its value is to conduct a set of sensitivity simulations by matching the total generated dust emissions with dust climatology data. I can understand that the dust climatology data over the selected domain might not be readily available or requires more work to obtain. This study tries to constrain the value of C by comparing the simulated AOD and Angstrom exponent with AERONET data, which may introduce additional uncertainties to the estimated dust emissions since those optical properties are also heavily

affected by anthropogenic aerosols besides dusts. This limitation should be discussed somewhere in the paper. In addition, the simulated AOD/ Angstrom exponent should not be evaluated against the same set of AERONET data anymore since they are anyway highly correlated because of the approach taken in this study.

We agree C is a highly tunable parameter that is dependent not only on properties of the dust region of interest, but also the grid spacing chosen for the model simulation (because the wind speed would vary somewhat with grid spacing). Thus, basing C on climatology would not include adjustments needed for grid resolution. We believe our approach is appropriate and has been evaluated with independent measurements. We compared WRF-Chem simulated aerosol optical depth with MODIS level 2 AOD retrievals also. The WRF-Chem model significantly underestimates the MODIS retrieved AOD during 13-16 April 2010 (low dust emission period) which could be due to the uncertainties in anthropogenic aerosol emissions over the Indian region as also noted by the reviewer. However, both the WRF-Chem and MODIS AOD show similar spatial distributions during 17-22 April 2010 (high dust emission period) even though the model still underestimates MODIS AOD retrievals especially in the regions not influenced by the dust storm. The average MODIS and WRF-Chem AOD (550 nm) values in a sub-region (70°-80°E, 25°-30°N) affected the most by the dust storm are estimated as 0.80 ± 0.30 and 0.68 ± 0.28 , respectively. Despite the differences in absolute magnitudes, the model captured the spatial distributions of percentage changes in AOD between high and low dust emission periods well. Further details of this comparison can be seen in Kumar et al., (2014).

The authors evaluated the model results by using NO₂ column data from the OMI instrument, which also measures O₃ and SO₂. Both species are highly related to this study. I would suggest adding the evaluation of those two species to make the evaluation more solid. The evaluation also falls short with the lack of aerosol comparisons (by using observed dust or even PM_{2.5} or PM₁₀ concentrations). If those data are indeed not available, an acknowledgement that such a comparison has not been done is needed.

Such a comparison will definitely strengthen the model evaluation but is not attempted here for the following reasons. In the case of OMI tropospheric ozone retrievals, the averaging kernels show low vertical resolution in the troposphere with a degree of freedom in the order of ≤ 1 . The tropospheric averaging kernels peak between 5-7 km and thus retrievals have very low sensitivity in the lower troposphere, which is the region of interest in this study. OMI SO₂ retrievals also have a low sensitivity in the lower troposphere and are very noisy. Average OMI retrieved SO₂ planetary boundary layer (PBL) column amount values in our model domain are in the range of 0.5-1.0 DU, while the standard deviation of the noise in the OMI SO₂ product is reported to be about 1.5 DU. We have now added this information in section 3.2. An evaluation of the aerosol simulation with MODIS retrieved natural color image, aerosol optical depth, and Angström exponent, and CALIPSO retrieved extinction coefficient was discussed in the companion paper (Kumar et al., 2014) and a summary of that evaluation is given in section 4.1 of this paper.

Specific comments:

Page 1116, line 22-26: I don't think this re-noxification process is a recent finding, since it has been reported in much earlier studies such as Knipping and Dabdub (2002).

We revised the text and now state that the renoxification process has been known for about 15 years but was not considered in global models.

Page 1117, line 4: for “absorbed phase”, should “aerosol phase” be more accurate?
We changed “absorbed phase” to “particle phase”.

Page 1118, Section 2: More information should be provided in this section regarding WRF/Chem model configurations (e.g., model inputs and physical/chemical schemes) and dust emissions schemes in this section since this is standalone paper.

We have now added the following information about model configuration in Section 2. “The static geographical fields such as terrain height, vegetation fraction, soil properties and land-use etc. are interpolated from 10 min (~ 19 km) United States Geological Survey (USGS) data to the model domain by using the WRF preprocessing system (WPS). The initial and lateral boundary conditions for the meteorological fields are obtained from the National Center for Environmental Predictions (NCEP) Final Analysis (FNL) fields available every 6h at a spatial resolution of $1^{\circ} \times 1^{\circ}$. The resolved scale cloud physics is represented by the Thompson microphysics scheme (Thompson et al., 2004) and sub-grid scale effects of convective and shallow clouds are parameterized according to the Kain-Fritsch convective scheme (Kain, 2004). The short- and long-wave radiative processes in the atmosphere are represented by the Rapid Radiative Transfer Model (RRTM) (Mlawer et al., 1997). For surface processes, the model setup uses the NOAH Land Surface model (Chen and Dudhia, 2001) and MM5 similarity scheme (Beljaars, 1994). The vertical sub-grid scale fluxes due to eddy transport in the planetary boundary layer (PBL) and the free troposphere are parameterized according to the Yonsei University (YSU) boundary layer scheme (Hong et al, 2006). Four dimensional data assimilation (FDDA) is applied to limit model errors in the simulated meteorological fields (Lo et al., 2008)”. Further details on dust emissions are also added following your comment on description of dust emission scheme.

Page 1118, line 8: need some details regarding this bulk aerosol scheme such as the aerosol size distribution, aerosol speciation, and major aerosol processes such as condensation and aerosol thermodynamics etc.

We have now added the following information in Section 2. “The GOCART model simulates five major tropospheric aerosol types including sulfate, organic carbon, black carbon, dust and sea-salt, and all aerosol components are assumed to be externally mixed. The GOCART model does not have an aerosol thermodynamics module. The emissions of sea-salt (four size bins) and dust aerosols (five size bins) are calculated online within the model.”

Page 1118, the description of dust scheme, line 15: how is S determined? line 18-19: the formula for ut should be provided; line 19: Are there any physical meaning of C or is it simply a tuning factor? A factor of magnitude difference seems to me to too very large.

S represents the fraction of alluvium available for wind erosion in a grid cell. In principle, S should be based on observations of alluvium in the model domain but such observations do not exist. Therefore, S is obtained by comparing elevation of each grid cell with its surrounding hydrological basin spread over an area of $10^{\circ} \times 10^{\circ}$. Thus, S does not provide

the exact amount of alluvium present but it provides information about the most probable locations of sediments. The map of S is then compared with a vegetation map derived from Advanced Very High Resolution Radiometer (AVHRR) data (DeFries and Townshend, 1994) and only the bare soil surfaces are considered as possible dust sources. In WRF-Chem, the source function is provided as an input static geographical field through the WRF preprocessing system (WPS).

The threshold wind velocity u_t is from the GOCART formulation (Ginoux et al., 2001):

$$u_t = \begin{cases} A \sqrt{\frac{(\rho_p - \rho_a)g\Phi_p}{\rho_a}} & (1.2 + 0.2 \log_{10} w), \quad \text{if } w < 0.5 \\ \infty & \text{otherwise} \end{cases} \quad (1)$$

where $A = 6.5$ is a dimensionless parameter, w is the surface wetness (0.001-1), Φ_p is the particle diameter, g is the acceleration of gravity, ρ_a and ρ_p are the air and particle density respectively. Further information about S and u_t can be obtained from Ginoux et al. (2001)

C is a tuning factor and does not have physical meaning. A factor of magnitude difference in the value of C results partly from the use of analysis nudging in this study as nudging leads to lower wind speeds. A sensitivity experiment showed that similar dust emission can be obtained with a C value of $9 \times 10^{-9} \text{ kg m}^{-5} \text{ s}^2$ without applying grid nudging, which is still 9 times higher than the C value proposed initially ($1 \times 10^{-9} \text{ kg m}^{-5} \text{ s}^2$) by Ginoux et al. (2001). However, we chose to use analysis nudging as the model configuration with analysis nudging is found to better reproduce the variations in observed aerosol optical properties as compared to one without analysis nudging (not shown). We added this information to the revised section 2.

Page 1119, line 1-5: A brief description regarding all those information should be provided, since this is a standalone paper.

We have now added the following information in Section 2. “Anthropogenic emissions of CO, NO_x, SO₂, NH₃, OC and BC and non-methane volatile organic compounds (NMVOC) are taken from the MACCity emission inventory (Granier et al., 2011) and emissions for PM_{2.5} and PM₁₀ are taken from the Intercontinental Chemical Transport Experiment – Phase B (INTEX-B) inventory (Zhang et al., 2009). Daily varying emissions of trace species from biomass burning are taken from the Fire Inventory from NCAR version 1 (FINN v1) (Wiedinmyer et al., 2011) and distributed vertically in the model following the online plume-rise module (Freitas et al., 2007). Note that FINN v1 accounts only for open biomass burning and the residential biomass burning is included in anthropogenic emissions. Biogenic emissions of trace species from terrestrial ecosystems are calculated online using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.04 (Guenther et al., 2006). The aerosols are allowed to provide feedback to the radiation scheme in the simulations but through direct effects only.”

Page 1119, line 19-20: How about aerosol nitrate and ammonium? Are they treated at all? Such information is expected when mentioning GOCART bulk aerosol module earlier.

The GOCART model in WRF-Chem does not treat nitrate or ammonium aerosols.

Page 1125, line 7: how is gamma determined for this Dust_JH_NO3_SO4 simulation?

In this simulation, we consider three reactions of ozone with dust: fresh dust particles, dust particles coated with nitrate, and dust particles coated with sulfate. The original γ value is used for reactions with fresh dust particles, while the original γ value is reduced by 70% for reactions with dust particles coated with nitrate and is increased by 33% for reactions with dust particles coated with sulfate. This information has been added to the revised section 2.4.

Page 1126, Section 3.2: Are level 2 or level 3 retrievals used?

We use Level 2 retrievals.

Page 1128, line 11: any reasons for the increase of NO_y during the indicated time period? Doesn't dust storm supposed to decrease the total NO_y?

We analyzed back air trajectories arriving at Nainital using the Meteorological Data Explorer (METEX; <http://db.cger.nies.go.jp/metex/>) during 15-19 April 2010. The trajectory plots are shown in the Figure below. METEX uses NCEP/NCAR reanalysis available every 6 hours at a horizontal grid spacing of 2.5°x2.5° data as its input. It is seen that air masses arriving at Nainital on 15-16 April passed over relatively cleaner regions and traveled at higher altitudes. From 17 April onwards, air masses traveled at lower altitudes and passed over the Indo-Gangetic Plain region before arriving at Nainital. This led to an increase in NO_y mixing ratios at Nainital on 17-18 April. Dust loading was also lower at Nainital on 17-18 April but increased 2-3 times on 19 April and that likely initiated the decrease in NO_y levels at Nainital. This information has been added to the revised section 4.1.

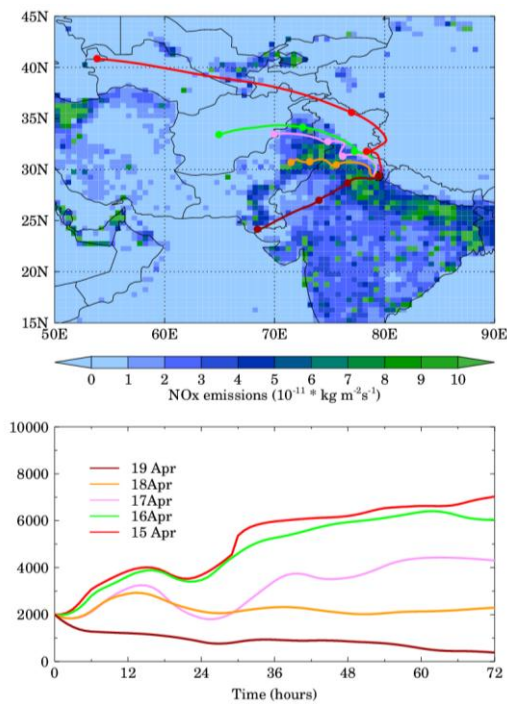


Figure: Top panel shows the spatial distribution of anthropogenic NO_x emissions and 3 day back air trajectories arriving at Nainital during 15-19 April 2010. The bottom panel shows the altitude attained by the back air trajectories.

Page 1134, Section 4.5: The paper examined the effects of RH on gamma values, which is not commonly considered by other regional models and the effort is appreciated. However, the gamma values associated with various RH values in this study differs around one order of magnitude or less, which is generally less than uncertainties of gamma values reported by literature. A set of sensitivity runs by using lower and upper bounds of gamma values would be more of scientific interests and can provide a range of estimate of impacts of dust associated heterogeneous chemistry on regional chemistry over the modeling domain.

We have conducted two sensitivity runs with lower and upper bounds of γ values reported in the literature. The results from these sensitivity runs are now discussed in a new section (4.6) called “Effects of uncertainty in reactive uptake coefficient (γ)”.

Page 1139, line 22-23: how about measurements of aerosols?

We mentioned the necessity of measuring physical and chemical properties of dust aerosols in line 24.

Fig. 10: what about the decrease and increase over northeastern corner of the domain in both NO₃ and SO₄ coating simulations? This needs to be clarified.

We acknowledge the reviewer for pointing this out as we found an error in plotting and apologize for the mistake. This figure is updated in the revised manuscript. Now, we do not see this increase and decrease in the northeastern corner of the domain and results are consistent with the distribution of dust loading in the domain with the highest changes in the Thar Desert and western Indo-Gangetic Plain region.

Technical notes:

Page 1122, line 5: H₂ should be HO₂?

Changed.

Page 1125, line 5: 70% in?

Changed.

Page 1130, line 17: the largest. There are other similar typos and should be fixed.

Changed. We fixed other typos as well throughout the manuscript.

Page 1130, line 20: I suggest using O₃ to denote ozone throughout the text to be consistent with other gases.

Changed.

Page 1131, line 25: likely less

Changed.

Page 1134, line 10: double check the range, I think it should be in the range of 70-90%.

Changed.

Page 1135, line 14: Dust_JH_NO3.
Changed.

References

- Dey, S., Tripathi, S. N., Singh, R. P., and Holben, B. N.: Influence of dust storms on aerosol optical properties over the Indo-Gangetic basin, J. Geophys. Res., 109, D20211, doi:[10.1029/2004JD004924](https://doi.org/10.1029/2004JD004924), 2004.**
- DeFries, R. S., and Townshend, J. R. G.: NDVI-derived land cover classification at a global scale, Int. J. Remote Sens., 15, 3567-3586, 1994.**
- Prasad, A. K., and Singh R. P.: Changes in aerosol parameters during major dust storm events (2001–2005) over the Indo-Gangetic Plains using AERONET and MODIS data, J. Geophys. Res., 112, D09208, doi:10.1029/2006JD007778, 2007.**