Comments by Referees are in blue. Our replies are in black. Changes to the manuscript are highlighted in red both in here and in the revised manuscript.

## Reply to Ref #1

This study reports room temperature uptake coefficients of chlorine nitrate (ClONO2) on TiO2 and SiO2 aerosol particles as well as on a macroscopic Pyrex surface. ClONO2 is implicated in the chlorine activation cycles sustaining stratospheric ozone loss and the formation of the polar ozone hole. This study is motivated by the proposals to use the injection of highly refractive nanomaterials, such as TiO2, into the stratosphere as a climate engineering measure to reduce solar radiation on the ground. Adding a substantial amount of TiO2 to the stratosphere is directly increasing the surface area for those heterogeneous processes normally occurring on polar stratospheric clouds or sulfuric acid particles of volcanic origin. ClONO2 hydrolysis is one of the key processes therein. Therefore, this study is addressing a highly relevant topic. The potential adverse (chemical) effects of solar radiation management schemes need careful attention. Apart from the laboratory measurement of the uptake coefficients, a global chemistry-climate model is used to assess the impact of TiO2 on stratospheric ozone in comparison to the sulfuric acid particle injection following the eruption of Pinatubo by tuning the TiO2 injection to have the same radiative properties as the Pinatubo sulfuric acid particles.

The results demonstrate uptake coefficients on TiO2 in the range of 1e-3 in the lower relative humidity range, which is significantly lower than hydrolysis on liquid sulfuric acid. For SiO2, uptake coefficients remained in the few 1e-4 range, about an order of magnitude larger than those observed on Pyrex, indicating the importance of representing the material of interest in the form most relevant for the atmosphere. The model work showed that injecting TiO2 into the stratosphere leads to two partially counteracting effects due to the altitude dependence of the efficiency of different species families involved in catalytic ozone loss: While the uptake of ClONO2 on TiO2 leads to less chlorine activation than would occur on sulfuric acid, the concomitantly smaller N2O5 uptake on TiO2 than on sulfuric acid results in lower ozone levels in the middle stratosphere. Therefore, within the constraints of a still not sufficiently established heterogeneous chemistry scheme, the effect of TiO2 on column ozone abundances remained similar to those of an equivalent sulfuric acid injection.

This study is well designed and performed and uses state of the art methods to address the kinetics of heterogeneous reactions. ClONO2 is an inherently difficult species to work with, and the efforts of the authors to synthesize, measure and calibrate it are appreciated. Only a few minor issues may remain as additional discussion topics with respect to the experimental part of the work. The model runs appear to be well designed, even though this reviewer is not familiar enough with modelling to judge the details. The manuscript is generally well written. A few comments below indicate where the structure could be improved.

**Author reply:** We would like to thank Ref #1 for his/her highly positive comments on our manuscript. All the comments have been properly addressed in our revised manuscript, as detailed below.

**Specific comments**

1. Introduction section: the authors should somewhere address the fact that TiO2 is a well-known photocatalyst, which may trigger radical production and chemical conversions, both oxidation and reduction. Are there estimates whether this could be relevant? Also, the photochemical activity is strongly size dependent and restricted to the size range used in this study. The authors should clarify whether the type of material studied here would be the one foreseen for the solar-radiation management purpose.

**Author reply:** This comment is very insightful. However, the effects of heterogeneous photochemical reactions (of $TiO_2$ and other potential SRM materials) on stratospheric chemistry have never been studied, and we are unfortunately unable to foresee a material for SRM. To make this clearer, the last sentence in the third paragraph of the introduction section has been expanded (page 4-5, line 87-89): "$TiO_2$ is an active photo catalyst (Shang et al., 2010; Chen et al., 2012; Romanias et al., 2012; Kebede et al., 2013; George et al., 2015) and the effects of its photochemical reactions on stratospheric chemistry, if injected into stratosphere for the purpose of climate engineering, are unknown. Therefore, its atmospheric heterogeneous photochemistry deserves further investigation."

2. section 4.1: since the measured uptake coefficient were rather close to the diffusion limit, the relevance of these values is rather limited. This section could therefore be condensed a bit. I suggest to add either the effective (uncorrected) uptake coefficients or the correction factor to table 1, so that the magnitude of correction becomes immediately apparent.

**Author reply:** We agree that the relevance of Section 4.1 is quite limited. Section 4.1 only contains two paragraphs and is difficult to be further shortened. We agree to include the effective uptake coefficients in Table 1. This has been done in the revised manuscript, and the table caption and related contents in Section 4.1 (page 17, line 386-387) have been updated accordingly.

3. page 17, lower paragraphs: while I agree that the local diffusion around the particles is not having an effect, I wonder whether the obviously strong radial gradients have an impact on the measured uptake coefficient. The effective first order wall loss rate coefficient is only acting on the average concentration.

**Author reply:** The referee is correct, and in fact this effect has been corrected. In the revised manuscript (page 18, line 409-411) we have added one sentence for explanation: "Axial and radical diffusion of $ClONO_2$ could lead to biases in its measured loss rates in a flow tube, and this effect, though very small (<10% in our work), has been corrected (Brown, 1978)."

4. page 20, top paragraph: it is not surprising that $ClONO_2$ hydrolysis behaves differently than $N_2O_5$ hydrolysis. However, from the discussion given here, it is not becoming apparent in what way the authors think the two mechanisms are operating such that $ClONO_2$ hydrolysis behaves as observed. Both processes

are likely initiated by OH groups, and both require adsorbed water. Is it maybe because for $N_2O_5$ two steps are required?

**Author reply:** Our measurements found that $\gamma(ClONO_2)$ is larger for $TiO_2$ but $\gamma(N_2O_5)$ is larger for $SiO_2$. We have realized our initial explanation is ambiguous. Therefore, in the revised manuscript we have changed the last sentence of this paragraph (page 21, line 483-486) to "This may indicate that a different mechanism controls $N_2O_5$ uptake by mineral surfaces. However, mechanistic explanations of the different heterogeneous reactivities of $N_2O_5$ and $ClONO_2$ on $TiO_2$ and $SiO_2$ surface at the molecular level cannot be derived from our data."

5. page 20, section 4.4 first paragraph: if Molina et al. have not done any control experiments in absence of HCl, I suggest to reduce this comparison to a minimum. It is rather trivial that the uptake on TiO2 in absence of HCl is different to that on alumina in presence of HCl. So there would be simply no data to compare with. In turn, the temperature dependence may indeed be important and should be carried into the modelling study as a big uncertainty.

**Author reply:** We agree with Ref #1 that it is expected that the presence of HCl will affect heterogeneous chemistry in the stratosphere. Nevertheless, we believe that it could be beneficial for a general audience to discuss the work carried out by Molina et al. in some details.

We also agree that the temperature dependence may cause large uncertainties. This is addressed together with next comment (point 6) raised by ref #1.

6. page 23, top paragraph: somewhere here the authors should address the sensitivity of the model runs to the temperature dependence of the uptake coefficient. I am not convinced that the studies cited for other species are giving a good indication for the potential T dependence for $ClONO_2$.

**Author reply:** We agree that our indication for potential temperature dependence is highly uncertain. In addition, sensitivity studies will be presented in a coming modeling paper. Therefore, in the revised manuscript we have rephrased the last sentence (page 24, line 567-571): "However, it is unclear whether temperature would have a significant effect on $\gamma(ClONO_2)$ for $TiO_2$ particles, and therefore our simulated impact of heterogeneous reaction of $ClONO_2$ with $TiO_2$ on stratospheric chemistry may have large uncertainties. The sensitivity of simulated stratospheric compositions to $\gamma(ClONO_2)$ for $TiO_2$ particles will be investigated in a following paper."

7. page 24, last part of discussion of modelling section: it is not clear to this reviewer what level of detail is included for the treatment of polar ozone, the occurrence and composition of PSCs etc. A few times, particularly strong effects at high latitudes are mentioned. It might be insightful to learn about the reasons for differences at high latitudes.

**Author reply:** As suggested, a description of modelled polar processes, and appropriate references, has been added to section 3 of the manuscript (page 14, line 320-324).

8. section 6: this section is not written as a conclusion. This is more a reiteration of the discussion and is partially repetitive. I suggest to integrate the important points to the previous sections and condense the rest into a real conclusion section. And since this rest contains quite a bit of statements and suggestions, I would entitle it as 'conclusions and outlook'.

**Author reply:** Indeed Section 6 includes some statements and suggestions, and as suggested, in the revised manuscript we have change its title to "Conclusions and outlook". We also agree that this section is partially repetitive. Nevertheless, we believe this information is appropriate in this section for those readers who may only briefly look at this study.

**Technical comments**

Page 2, abstract, line 20: revise sentence: 'Introduction of . . .would scatter solar radiation'; it is the particles that have an effect, not the introduction!

Page 7, line 160: . . .was then passed through. . .

Page 9, line 208: . . .served as a dry atmosphere. . .

Page 18, line 421: . . .The heterogeneous reaction . . .was studied. . .

Page 19, line 456:. . .adsorbed water on the $SiO_2$ surface. . .

Page 22, line 527:. . . has a much smaller impact . . . than. . .(not 'reduced impact')

Page 23, line 558: In contrast, . . .

**Author reply:** We would like to thank Ref #1 for carefully reading our manuscript. All the typos have been corrected in the revised manuscript.

Comments by Referees are in blue. Our replies are in black. Changes to the manuscript are highlighted in red both in here and in the revised manuscript.

**Reply to Ref #2:**

Summary. Due to its high refractive index, $TiO_2$ has been considered as a geoengineering material that could be deliberately injected into the upper atmosphere for the purpose of scattering incoming solar radiation. However, the consequences of this added aerosol mass on heterogeneous reactions that impact ozone levels in the stratosphere are unknown. Tang et al. present a combined experimental and modeling studied aimed at understanding the effects of injected $TiO_2$ particles on stratospheric chemistry, with a focus on heterogeneous hydrolysis of chlorine nitrate ($ClONO_2$), a process known to activate Cl and lead to stratospheric ozone depletion. Tang at al. use an aerosol flow tube technique with chemiluminescence detection of $ClONO_2$ (and associated aerosol sizing / number measurements) to study the loss of $ClONO_2$ on $TiO_2$ particles. For comparison, losses onto $SiO_2$ aerosols are also studied, in addition to the adsorption of $ClONO_2$ to the flow tube walls. Ambient temperature uptake coefficients for $ClONO_2$ are reported over a limited relative humidity range.

It is clear to this reviewer that a lot of hard work that went into making these measurements; they are not easy. Generating a flow of $ClONO_2$ that is free of impurities, the constant supply of uniformly sized aerosols that is required, and the method of indirectly detecting $ClONO_2$ via catalytic decomposition followed by chemiluminescence detection are complex and present multiple challenges. The methods appear to be appropriately chosen and the experiments executed in the best possible way. The main weakness in the experiments is that wall uptake was so high that in some cases, wall losses masked uptake onto the aerosol particles; this likely contributed to the limited scope of the data presented.

A unique aspect of the work is its use of modeling to evaluate the impact of the measured $ClONO_2$ uptake coefficients on a hypothetical event where $TiO_2$ or sulfate aerosols are injected into the stratosphere. A vertically resolved global chemistry-climate model (UKCA) indicated that less ozone destruction occurred as a result of reactions of $ClONO_2$ and $N_2O_5$ on injected $TiO_2$ particles vs. on aerosols formed from the Mt. Pinatubo eruption (under conditions where both injection events had the same solar radiation scattering). My comments are listed below.

**Author reply:** We would like to thank Ref #2 for his/her positive comments on our manuscript. All the comments have been properly addressed in the revised version, as detailed below.

1. General Comments. The description of $ClONO_2$ generation and detection is detailed in the methods section, but at times it is difficult to reconcile with Figure 1. I recommend that more detail be added to Figure 1 to show the aerosol cyclone mentioned, two diffusion driers, and the reactor that converts $ClONO_2$ to NO, etc. In addition, it would benefit the reader, especially when reading section 2.1.3, to include a diagram of the $ClONO_2$ detection scheme.

**Author reply:** In the revised manuscript the following changes have been made:

1) As request, in our revised manuscript we have updated Figure 1 to include the cyclone and how we mixed a NO flow with the sampled $ClONO_2$ flow. It should be pointed out that diffusion dryers were included in our initial figure.

2) Scheme 1 has been added in the revised manuscript to explain our $ClONO_2$ detection scheme (page 37). Accordingly a sentence has been added in Section 2.1.3 (page 10, line 227-228): "The scheme used in our work to detect $ClONO_2$ is shown in Scheme 1 and explained in detail below."

2. I feel that the rationale for choosing the $ClONO_2$ uptake coefficients used in the model was not made sufficiently clear. Uptake coefficients for both $N_2O_5$ and $ClONO_2$ hydrolysis on stratospheric $TiO_2$ particles are set to 0.0015. The $N_2O_5$ value of 0.0015 is taken from the group's prior work (Tang et al. 2014d). It is not clear why the authors assume the uptake coefficient for $ClONO_2$ is the same as that of $N_2O_5$. The values for gamma($ClONO_2$) listed in Table 2 for $TiO_2$ are 0.001, so I am assuming that given the error in the measurements the authors are just assuming that the uptake coefficients are the same within error for the two processes?

**Author reply:** The referee is correct. In our revised manuscript we have added one sentence to make this clearer (page 16, line 365-367): "Considering errors in measurements, this value agrees with experimental $\gamma(ClONO_2)$, which was determined to be ~$1.2\times10^{-3}$ in our work as shown in Table 2."

3. I feel that the $TiO_2$ uptake coefficient for $ClONO_2$ may be underestimated, meaning the ozone loss predicted by the model may be underestimated. The studies here were conducted at room temperature and lower temperatures expected for the stratosphere could result in higher gamma-values. The authors discuss this near line 549 and argue that the measured room temperature gamma-values may be within a factor of 2 or 3 of those at lower temperatures. More important may be the concentration effect. A concentration dependence of the uptake coefficient for the reaction of $ClONO_2$ on $TiO_2$ surfaces is an important consideration that should be addressed in a revised manuscript. One would expect significant surface saturation at the high concentrations (hundreds of ppb) used in this study. This effect would result in correspondingly low uptake coefficients. $ClONO_2$ levels in the stratosphere are 2-3 orders of magnitude lower than the concentrations used in this study. Therefore, it is likely that the uptake coefficients under atmospheric conditions of lower $ClONO_2$ concentrations would be higher than those reported. Related to this, I feel it is important to list specific $ClONO_2$ concentrations used in each experiment listed in Table 1 and 2.

**Author reply:** We agree that low stratospheric temperatures will affect the measured $\gamma$ values. This is addressed in our reply to Ref 1 (point 6). We agree with the referee that the dependence of $\gamma(ClONO_2)$ on $ClONO_2$ concentrations could be significant. We have made the following changes in the revised manuscript:

1) In Section 4.2 we have added the following sentences to address the possible effect of $ClONO_2$ concentration on $\gamma(ClONO_2)$ (page 19, line 438-441): "It should be pointed out that our measurements were carried out with $ClONO_2$ mixing ratios of several hundred ppbv, significantly higher than those found in the lower stratosphere. Therefore, our measurements could underestimate $\gamma(ClONO_2)$ under stratospheric conditions."

2) In captions of Tables 1 and 2, we have included initial $ClONO_2$ mixing ratios used in our work. Because $ClONO_2$ concentrations in each experiments were very similar, we do not list them individually.

4. How relevant is it to consider adsorption to a $TiO_2$ surface, which at room temperature and at 7-33 % relative humidity would contain a monolayer (or less) of adsorbed water? In the stratosphere, I would think that injected $TiO_2$ particles would be rapidly coated in NAT, HCl, $H_2SO_4$, etc. If that is true, should not the model be treating the $TiO_2$ as simply a seed particle? Or does it already? In that case, would it not be more accurate to assume that the uptake coefficients would be those for $ClONO_2$ uptake onto PSC components, which could be one or two orders of magnitude higher than what was measured in this work on $TiO_2$?

**Author reply:** The referee has raised a critical question on stratospheric particle injection. We agree that if a material (e.g., $TiO_2$ considered in our work) was injected into the stratosphere, it may be coated by $H_2SO_4$, NAT, water ice, and etc. However, assessing these microphysical aerosol processes is beyond the scope of the modelling experiments performed here. In Section 6, we have added the following sentences to emphasize this issue (page 27, page 636-640): "In this work we have only considered heterogeneous chemistry of fresh $TiO_2$ particles. If injected into the stratosphere, $TiO_2$ particles would likely be coated with $H_2SO_4$, NAT, water ice, etc., and heterogeneous reactivity of coated $TiO_2$ particles could be very different from fresh particles. This important issue should be addressed by further laboratory and modeling studies."

5. Lastly, I am aware of the meaning of the word "nudged" in the context of atmospheric models. However it is ambiguous and could be misinterpreted by a non-scientist who could think "nudging" a model means to coax it into giving you the results you want to see (thinking of "Climategate here). I would encourage the authors to consider replacing a phrase like, ": : :simulations were nudged: : :" with something more accurate; for example, ": : :initial conditions were set to: : :"

**Author reply:** We thank the reviewer for their comment. As the reviewer states, nudging is a technical term that deserves better definition in the text. We have amended the text to give a fuller definition of what is meant by the term nudging in the text and supplied appropriate references as well (page 14-15, line 329-335). However, as it is a technical term which describes part of the model set-up used in this study, we feel it is necessary to include this term in our discussion.

Specific Comments:

line 279: replace "spectroscopy" with "spectrometry."

**Author reply:** Corrected.

line 540-542: It is not clear to me how the presented "measurements suggest that the uptake coefficient onto $TiO_2$ is smaller than that for sulphate below ~215K." This comment is related to the discussion above regarding the relevance of treating $TiO_2$ as pure $TiO_2$ surface or one that coated and has surface properties more in line with a PSC.

**Author reply:** In the revised manuscript we have change "onto TiO2" to "onto fresh $TiO_2$". We have also provided a few sentence in Section 6 to discuss the relevance of coating on $TiO_2$, see our reply to comment 4.