

The comments from the editor (also referee #2) are in blue, and our replies are in black.

The major changes to the manuscripts are highlighted in red in both the manuscript and this reply.

Thank you for your contribution to ACP. Unfortunately one Referee did not submit a report in time, so I provide a quick review to substitute a report of one Referee.

The manuscript describes the uptake of N₂O₅ to TiO₂ aerosol and the impact of this on stratospheric N₂O₅ and ozone budgets. Such studies are highly relevant and needed to understand the consequences of recently proposed approaches of solar-radiation management. The study is carefully done and analysed, conclusions are well justified and limitations are highlighted. Even though it is not a complete study, I accept this manuscript for publication in ACP after some minor changes.

Reply: We would like to thank the editor for his time spent on our manuscript, and his positive comments.

There are three main aspects that I ask you to discuss in more detail: * Could you give more details on the humidity and temperature conditions in the stratosphere for the altitude that shows highest TiO₂ concentrations after injection. This would help the reader to relate your experimental study to the relevant environmental conditions. I feel that currently the relevance of the experimental settings is addressed rather late in the manuscript and the reader keeps wondering why you did experiments at RT and whether or not the RH are appropriate for the stratosphere.

Reply: It is a very good point. In the last paragraph of Page 4425 (ACPD) we have added a few sentences to explain it: “We note that in lower stratosphere the typical temperature and RH ranges are 200–220 K and <40 %, respectively (Dee et al., 2011). While our experimental work covers the RH range relevant for the stratosphere, it has been carried out at room temperature instead of ~200 K due to experimental difficulties.”

* You nicely show and discuss the dependence of N₂O₅ uptake on relative humidity and conclude that the water at the TiO₂ surface is relevant. Taken that temperature is lower in the stratosphere than at RT (where I assume the Goodman, 2001, data were derived); how would the water coverage look like at stratospheric temperatures; is that known?

Reply: The surface coverage of H₂O depends first on relative humidity (RH), and probably also temperature; however, data at low temperature is not available. At the end of section 3.2 we have added a few sentences to explain it: “The surface coverage of water is determined by RH, and is probably also affected by temperature. However, the RH-dependent water surface coverage has only been investigated at room temperature but not under lower stratospheric conditions (200-220 K).”

* What is the effect of N₂O₅ ↔ NO₃ + NO₂ equilibrium on your results. Removing N₂O₅ by uptake might lead to re-formation from NO₃ and NO₂. Did you by-pass the 100 °C reaction chamber occasionally to observe changes in NO₂?

Reply: The NO_x analyzer used in this work could not differentiate NO₂ and N₂O₅, because they both (if the 100 °C reactor is bypassed) will be converted in the catalytic convertor to NO which is then measured by the chemiluminescence method. It is why in this work we use an indirect method to measure N₂O₅ by measurement of the NO change.

The effect of this equilibrium on the N₂O₅ uptake measurement has been discussed in details by Tang et al. (2012). In the revised version we briefly discuss this effect at the end of section 3.1: “The recombination of NO₂ with NO₃ (R4a) leads to the formation of additional N₂O₅, and the removal of NO₃ by the aerosol and wall surface causes further removal of N₂O₅ (R4b). Wagner et al. (2008) and Tang et al. (2010) simulated the effects of these reactions on N₂O₅ uptake measurement, and concluded that at room temperature the influence is negligible.”

Further, I hope you’ll find the following detailed comments helpful: P4424 115ff: Reword: This implies a connection between low stratospheric ozone and decrease in surface temperature.

Reply: In the revised version we have revised it to “The eruption of Mt Pinatubo introduced an additional 30 Tg of aerosols into the stratosphere. This increased aerosol loading resulted in surface cooling and produced record low levels of stratospheric ozone (Dutton and Christy, 1992; McCormick et al., 1995).”

P4428, 120 ff: Could you include some more details about the experimental set-up such as concentration. What does "largely reduce NO₂" mean exactly.

Reply: In L12-13, Page 4429 of the ACPD paper, we have changed the sentence to “This procedure was found to largely reduce the NO₂ impurity which was not completely oxidized by O₃ and thus also trapped in the cold finger at -76 °C during the N₂O₅ synthesis.” At the end of section 2.1.4, we have added a sentence to give the N₂O₅ concentration used in our study: “The initial N₂O₅ mixing ratios used in the flow tube were in the range of 1-2 ppmv.”

P 4430 110: Wagner described this synthesis first, didn't they? Could you add a reference?

Reply: This scheme was developed by Fahey et al. (1985), and our work largely followed that described by Wagner et al. (2009). At the end of this paragraph we have added a sentence to acknowledge both studies: “This scheme has been suggested as an absolute method to calibrate other N₂O₅ detection methods (e.g., CIMS) (Fahey et al., 1985) and is widely used to study the heterogeneous reactions of N₂O₅ with aerosol particles (e.g., Wagner et al., 2008).”

P4433 19: "The difference of k_w measured before and after introducing TiO₂ aerosols in the AFT was insignificant, indicating that the N₂O₅ wall loss did not change significantly during the uptake experiment." How much did it change usually, could you specify.

Reply: The change is within the experimental uncertainties. We have specified it in the revised version: “was within the experimental uncertainty associated with k_w determination.”

P4433 115. It is not clear what "true loss rate" means in this context, could you specify?

Reply: We have modified it in the revised version: “The direct derivation of loss rates from exponential decays (e.g., Fig. 3) assumes the plug flow condition and no radical/axial diffusion. However, under laminar flow conditions the flow is non-plug and axial and radical diffusion also contribute to the apparent (or experimentally derived) loss of N₂O₅; therefore, the true loss rate is different from the apparent loss rate.”

P4433 1 18+19: Change to Author (year)

Reply: We have changed it to “flow tube studies (e.g., Thornton et al., 2003)”.

P 4433 125: define gamma and gamma(eff) and gamma(exp)

Reply: In the ACPD paper we described the relation between γ and γ_{eff} . In the revised version we have added a sentence to define γ before we give the equation (2): “The rate of a heterogeneous reaction is usually described by the uptake coefficient, γ , which is equal to the probability that a gas molecule which collides with the surface is removed from the gas phase.”

P4437110: Why "Another"?

Reply: We have changed it to “The”.

P4439124 I don't understand this: ,“and this may be a result of an overestimate of surface area densities caused by extrapolation over the poles“

Reply: There are missing values in the observations used to construct the surface area density data set. Over the poles the missing values in the data set are filled by extrapolating the closest values. As with all extrapolations this produces an element of uncertainty, including spurious fluctuations. We have changed this sentence to “and this may be a result of overestimating surface area densities over the poles where have no observational data constraint.”

P4440110: "Whilst we acknowledge that there are limitations to these simulations, most notably the inclusion of only a single heterogeneous process on the TiO₂, but also due to factors such as the omission of the TiO₂ aerosols from the photolysis calculation, we believe the qualitative conclusions from them are valid." This sounds a little vague. Could you summarize why you believe this?

Reply: We have added a few sentences to explain further it: **We base this on our understanding of the atmospheric response to the eruption of Mt. Pinatubo. Here the dominant factor on the global stratospheric chemistry was the increased heterogeneous chemistry, with factors such as changes in photolysis rates being secondary. However, further studies are required on effects on changes in photolysis before any definite conclusions can be reached.**

P4441115: At what concentration did Molina 1997 study the uptake? Are those atmospherically relevant?

Reply: We have expanded this sentence to include more details of Molina et al. (1997) in the revised version: **One previous study (Molina et al., 1997) investigated the uptake of ClONO₂ ($1-10 \times 10^{-7}$ Torr) onto aluminum oxide and Pyrex glass in the presence of HCl ($1-10 \times 10^{-6}$ Torr) at 210-220 K, and suggested that this process is very efficient, with an uptake coefficient of 0.02, which is >10 times larger than that onto stratospheric sulfuric acid aerosols.**

P4442: What is QBC?

Reply: We have changed it to "**Quasi-Biennial Oscillation**".

P4445, Caption fig 4: could you add experimental settings?

Reply: Figure 4 presents the uptake coefficients measured in this work, and experimental details were given in the initial ACPD paper. Therefore we think that the editor asked for some experimental details of Goodman et al. (2001). In the revised version we have changed "reported by Goodman et al. (2001)" to "**measured by Transmission FT-IR spectroscopy (Goodman et al., 2001)**".

Section 3.1 and 3.2: What is the surface coverage of N₂O₅ and of H₂O? How important is the thermal N₂O₅-NO₂ equilibrium as source of uncertainties? Did you observe NO₂ upon N₂O₅ uptake, or do your data suggest that N₂O₅ is completely taken up (as 2 HNO₃) by the aerosol? Did this depend on humidity?

Reply: 1) Surface coverage of H₂O depends on RH, shown in Fig. 4 by citing the work of Goodman et al. (2001). N₂O₅ is converted to HNO₃ after uptake on the surface, so it may not have a surface coverage.

2) The effect of this equilibrium is addressed in a previous reply to your comment.

3) Unfortunately the detection used in this work does not have selectivity towards NO₂. However, Tang et al. (2012) confirmed that the formation of NO₂ in the N₂O₅ uptake is negligible. In the last paragraph of Page 4425 (ACPD), we have added a few sentences to make this clear: “Seisel et al. (2005) observed the formation of nitrate on mineral dust particles due to the uptake of N₂O₅ using diffuse reflectance FTIR, and Tang et al. (2012) further confirmed that the yield of nitrate is ~2 (as expected from R1) within the experimental uncertainty, and that the formation of NO₂ is negligible.”

Introduction or Discussion: Are there other important loss processes in the stratosphere, i.e. photolysis that might be changed by TiO₂ (and the induced changes on radiation). Could you elaborate on this?

Reply: We have modified Line 22-25, Page 4441 to discuss further heterogeneous photochemical reactions which might have some importance: “For example, the uptake of NO₂ on TiO₂ particles is enhanced under irradiation (Ndour et al., 2008; El Zein and Bedjanian, 2012), leading to the formation of HONO, the photolysis of which produces NO and OH and may perturb the stratospheric NO_x and HO_x cycles. Heterogeneous chemical oxidation of SO₂ could enhance the formation of sulfate coating on mineral particles (Shang et al., 2010).”

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