

Reply to referee #1

We thank referee #1 for their helpful comments on our paper. Below are our responses.

Page 20894, lines 24-26 A reference is helpful to support the use of a constant oceanic DMS concentration of 2 nM/L.

This was estimated from the database of Kettle et al. (1999), as mentioned in our companion paper (Archer-Nicholls et al., 2014). We will include the same reference in this paper too.

Page 20903, lines 24-26 Most air quality models employ 90% of NO_x as NO and 10% of NO_x as NO₂ or something similar. NO₂ fraction in new vehicle emissions is even greater. Is there any specific reason for using the entire NO_x as NO?

There was no specific reason for the NO_x emission speciation other than the substantial uncertainty in the inventory in this regard. To test the implications of our simplification we have run the “het on” scenario with all NO_x emissions (not only road traffic emissions) apportioned as 80% NO and 20% NO₂ (providing us with an extreme scenario to examine the influence of NO_x apportionment). The results from this model run along the flight-track for B541 are compared with measurements (and the results from the “het on” scenario used in the paper) in Figure 1. It can be seen for all chemical species that there is very little difference in the agreement between modeled and measured concentrations.

For future air quality studies, the apportionment of NO_x emissions is something to be addressed. The main focus of the current study is the investigation of whether N₂O₅ heterogeneous chemistry is required to replicate measured NO₃ and N₂O₅ mixing ratios (and so night-time oxidative chemistry). The lack of sensitivity to primary NO₂ emissions is clearly demonstrated by the indifference shown in Figure 1.

Page 20905, the last paragraph It is not clear how the low sulphate content of the PM1 aerosol in the model leads to higher PM1 chloride content. Please elaborate briefly.

This sentence is poorly worded. What we meant is that the modelled sulphate:ammonia ratio is lower than the measurements and hence the model chemistry is less ammonia-limited than in reality. The surfeit of ammonia means that there is enough available to neutralise the excess acidic sulphate (so that less chloride ions are displaced from sodium chloride). Similarly, the additional ammonia condensation will neutralise excess acidic nitrate, and chloride from hydrochloric acid. We will clarify the paper text to read:

“The lower sulphate to ammonium ratio of the PM1 aerosol in the model leads to the model chemistry being less ammonia-limited than in reality. This allows for a

higher PM1 chloride content in the model than was measured (model means of 0.1-0.4, compared with measurement means of 0.04-0.06 $\mu\text{g}/\text{kg}$, see Supplement). Generally this is in the form of sodium chloride, but for particles below a diameter of 0.3 μm (MOSAIC size bins 1-3) there is significant ammonium chloride as well, created by the co-condensation of hydrochloric acid with ammonia.”

Section 3.4 A figure presenting reaction probability will be helpful to readers.

We have drafted Figure 2 below to illustrate the dependence of the reaction probability on the mole ratio of $\text{H}_2\text{O}/\text{NO}_3^-$, chloride ion content, and organic mass fraction. This figure, and the following text, will be added to the end of Section 2.2 (where the scheme is described):

“The composition dependence of $\gamma_{\text{N}_2\text{O}_5}$ using this combined formulation is illustrated, for a 1 μm diameter particle, in Figure 1. The wholly inorganic, 10% (by molar content) chloride ion scenario (solid red line) gives a rough indication of the upper uptake limit, while the 30% (by mass) organic matter (OM) particle composition scenarios (all dotted lines) give a rough indication of the lower uptake limit.”

We would like to thank the anonymous referee for suggesting the inclusion of this figure. While creating it we discovered an inconsistency between our implementation of the suppression by organic components and that reported in the Riemer et al (2009) parameterization – we have changed this to be consistent with the Riemer et al (2009) paper and rerun the “organic suppression” scenario. Figure 3 illustrates the difference in uptake coefficient between the old parameterization (dashed lines) and new parameterization (solid lines). The effect of the change is to decrease the suppression of the N_2O_5 uptake coefficient by the organic shell. This is most evident for a low organic mass content (<10% OM); for higher mass contents, similar to those measured by the AMS during the RONOCO campaign (>20%, and generally around 30-40% OM), the difference between the two implementations is less significant.

The NO_3 , N_2O_5 , and HNO_3 mixing ratios predicted by the new “organic suppression” scenario during flight B541 are compared with those predicted by the “het on” and “het off” scenarios in Figure 4. The results from the new “organic suppression” scenario are much closer to the measurements than those of the “het off” scenario, however the “het on” scenario is still the best. The suppression of the N_2O_5 uptake coefficient is much less during the “organic suppression” scenario than that indicated by analysis of the AMS measurements (Morgan et al, 2014). This is because the OM mass simulated by the model is significantly lower (typically around 5% OM) than that measured during flight B541 (typically around 30% OM).

We will replace the “organic suppression” scenario plots in the Supplement with new plots generated with this more consistent parameterization. However, both because the inorganic only scenarios are a better fit to the measurements, and

because of the discrepancies in OM mass fraction between the model and measurements, we propose to not modify the main body of text to include discussion of the “organic suppression”, but instead to replace the sentence discussing the “organic suppression” scenario in the introduction to Section 3.4 with the following:

“The results from the “organic suppression” scenario were similar to those from the “het on” scenario, though the “het on” scenario results are generally a better fit to the measurements (see discussion below). The organic mass fractions of the aerosol in the model are significantly lower than those measured by the AMS instrument, resulting in far lower suppression of the N_2O_5 uptake coefficient than that calculated from the measured aerosol compositions (Morgan et al., 2014). Because of this discrepancy the results of the “organic suppression” scenario have been included in the Supplement, but are not discussed below.”

Section 3.5 The authors suggest that the daytime nitrate production is the main reason for over-predicting PM1 nitrate and HNO3 compared measurements. It will be helpful to readers to specify the rate constant used for the NO_2+OH reaction.

We use a three-body rate for NO_2+OH reaction. The low pressure rate coefficient is $2.6\text{e-}30\cdot(\text{T}/300)^{-3.2}\cdot[\text{M}]$, and the high pressure rate coefficient is $2.4\text{e-}11\cdot(\text{T}/300)^{-1.3}$ (after the recommendations of DeMore et al., 1994). This gives a similar, though not exactly the same, rate as would be derived from the latest IUPAC recommended values (Atkinson et al, 2004) (i.e., at 1 atmosphere of pressure, and a temperature of 285K, the reaction rate of NO_2+OH in CRIv2-R5 is $1.28\text{e-}11$, and is $1.25\text{e-}11$ when using the IUPAC recommended values).

We will add an extra sentence to Section 3.5 with this information, which will go after the sentence on lines 9 & 10 on Page 20912.

Section 3.5 How is the partitioning of nitrate between gas and aerosol phases accounted for in the model?

The partitioning of nitrate between gas and aerosol phase is calculated dynamically using the MOSAIC (Model for Simulating Aerosol Interactions and Chemistry) module (Zaveri et al, 2008). This uses the Multicomponent Equilibrium Solver for Aerosols (MESA; Zaveri et al, 2005) to calculate the phase state of the particles in each aerosol size bin (employing a temperature dependent mutual deliquescence relative humidity parameterization) and the composition (and phase state) dependent equilibrium partial pressures of HNO_3 (as well as HCl , and NH_3) over each of the 8 aerosol size bins. The dynamic partitioning of mass between the gas phase and the aerosol phases of each bin is then calculated using an adaptive time-stepping scheme, combined with a “dynamic pH” approach to the co-condensation of acids and ammonia. In box-model tests this approach has been shown to give results comparable to using a rigorous solver for integrating the stiff-ODEs, while having a comparable

computational efficiency to the equilibrium bulk partitioning model, ISORROPIA (see Zaveri et al, 2008, for benchmarking examples).

Page 20909 (lines 22-25) Table 3 suggests that the full inorganic N₂O₅ heterogeneous chemistry following Bertram and Thornton is employed for “het on” case while the “no cl pathway” case employs the inorganic N₂O₅ heterogeneous chemistry without the ClNO₂ production. If the “het on” case includes ClNO₂ production, then it should produce lower HNO₃/NO₃-prediction compared to that of “no cl case (since a fraction of the reaction produces ClNO₂). However, the authors state that “het on” produces more HNO₃ than the “no cl pathway” case which is contrary to the findings reported by Sarwar et al. (2012, ACP). Some discussions are needed.

The majority of nitrate produced by N₂O₅ heterogeneous chemistry remains in the particulate phase, rather than being outgassed as HNO₃. We do observe, during these particular scenarios, that the “het on” case has similar gas-phase HNO₃ mixing ratios to the “no Cl pathway” case. However significantly less particulate nitrate is produced during the “het on” case than the “no Cl pathway” case. Because gas-phase HNO₃ contributes less than 20% of the total nitrate in our simulations, this means that overall there is more nitrate formed in the “no Cl pathway” scenario than in the “het on” scenario, and so our findings do not contradict those of Sarwar et al. (2012).

To avoid confusion here we will modify the end of the sentence on lines 22-23 to read: “model predicted gas-phase HNO₃.”

Page 20910, lines 7-9 The following sentence is not clear: In all model scenarios, however, the potential PM₁₀ nitrate (HNO₃ plus PM₁₀ nitrate) is lower than the summed CIMS+AMS potential PM₁ nitrate (not shown).

What we intended to indicate with this statement was that the total amount of nitrate predicted at this location and time by the model was less than the measured nitrate (which was only in the gas-phase or in PM₁). This is because, if we had compared like with like (i.e. just the gas-phase HNO₃ and PM₁ nitrate) then it would have been possible to argue that the shortfall in modeled nitrate mass could be because the model was not correctly predicting the distribution of nitrate mass between PM₁ and large particles. By making this comparison it becomes clear that this cannot be (the only) cause for the shortfall in modeled nitrate mass in these particles.

We will add this sentence to the paper, after the sentence in lines 7-9, to make our point clearer:

“This shows that the shortfall in PM₁ nitrate mass within the model, compared with measurements, cannot only be due to the differences between the real and modelled aerosol size and composition distributions.”

Figure 12 Panels A and B show the incremental change in the domain mean total nitrate. However, it is not clear how the incremental change was calculated. Which height is shown in the figure?

Apologies – the label on the right-hand y-axis is rather misleading (there should be height tick marks, however the plotting package could not produce fine enough increments to be useful on these figures). We have removed “Height (km)” labels from the plots for the final paper. The pressure height is shown by the y-axis on the left of each panel.

The incremental change in the domain mean total nitrate is calculated in the following manner:

- 1) The incremental change in total nitrate in each grid cell, across the entire domain, between the current output file and the previous output file was calculated (model data is output every hour).
- 2) This data was then interpolated onto pressure levels (every 10 hPa from 1000 hPa up to 550 hPa).
- 3) Calculating the domain mean at each pressure level (throwing away the 10 grid cells around the edge of the domain, and removing NaN values where data doesn't exist in a given location for a given pressure level).

Technical corrections:

Page 20890, lines 11-12 The sentence starting with “Under this formulation ...” appears to be incomplete.

The reviewer is correct - this sentence should be connected with the sentence following it, rather than taking the rather disjointed form they have now. We will replace these two sentences with this text instead:

“Under this formulation $k'_{2f} = 0$ when a particle is completely dry ($[H_2O(l)]=0$). This gives $\gamma_{N_2O_5} = 0$, and so no N_2O_5 uptake will occur on dry particles.”

Page 20893, equation (7) $C_{N_2O_5}$ in equation (7) is not defined.

Apologies for missing this definition out. We will add the following text to the end of the first sentence on Page 20894:

“and $C_{N_2O_5}$ is the average velocity of $N_2O_5(g)$ in the gas phase.”

Page 20901, line 25 The sentence appears to contain an extra parenthesis following [NO₂].

The extra parenthesis has been removed.

Page 20902, line 13 Please check the subscript of N2O5.

We have corrected this typographic error.

References:

DeMore, W. B., Sander, S. P., Howard, C. J., Ravishankara, A. R., Golden, D. M., Kolb, C. E., Hampson, R. F., Kurylo, M. J., and Molina, M.: Chemical kinetics and photochemical data for use in stratospheric modelling, Evaluation Number 11, National Aeronautics and Space Administration, Jet Propulsion Laboratory, JPL Publication 94-26, 1994.

Sarwar, G., Simon, H., Bhave, P., and Yarwood, G.: Examining the impact of heterogeneous nitryl chloride production on air quality across the United States, *Atmos. Chem. Phys.*, 12, 6455-6473, doi:10.5194/acp-12-6455-2012, 2012.

Figures:

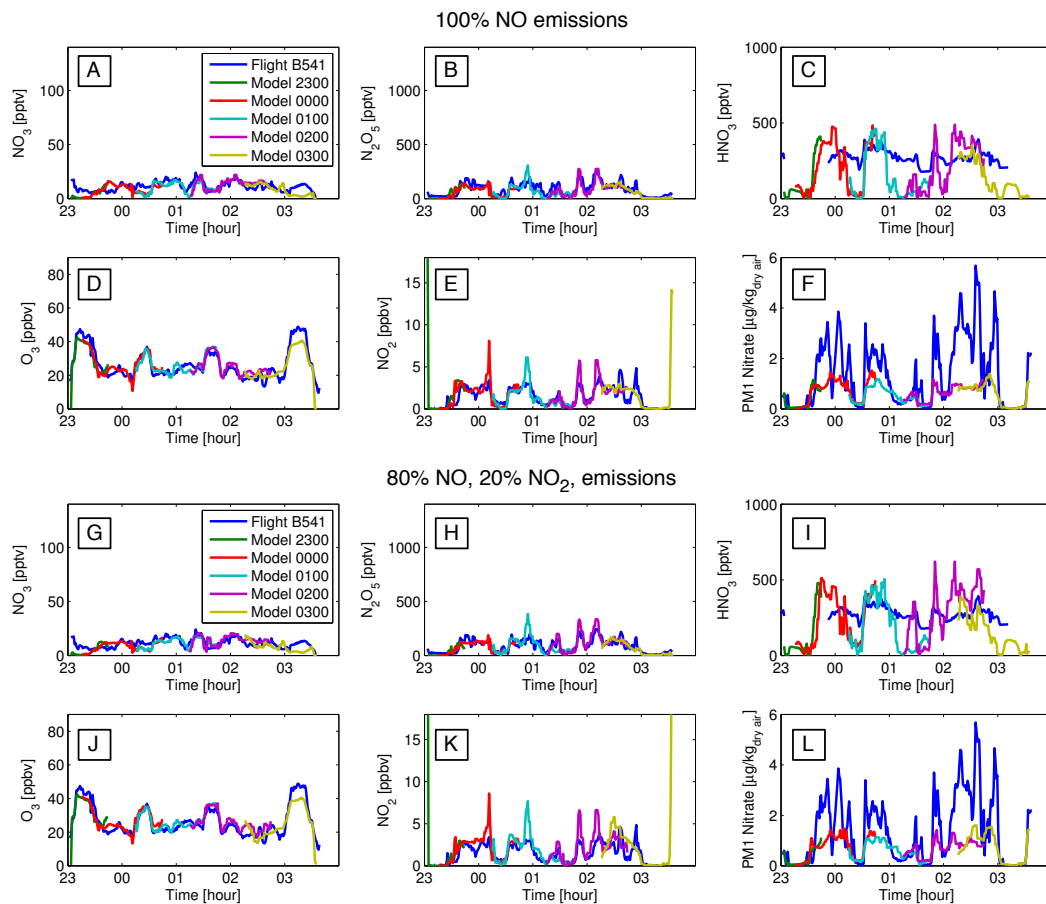


Figure 1: Flight-track measurement-model comparison during flight B541 for NO₃ (panels A and G), N₂O₅ (B and H), HNO₃ (C and I), O₃ (D and J), NO₂ (E and K), and PM1 nitrate (F and L). Plots show 1 min averaged measurements (blue lines), and data from the “het on” scenario run with NO_x emissions speciated as either 100% NO (panels A-F), or 80% NO and 20% NO₂ (panels G-L) (multicoloured lines).

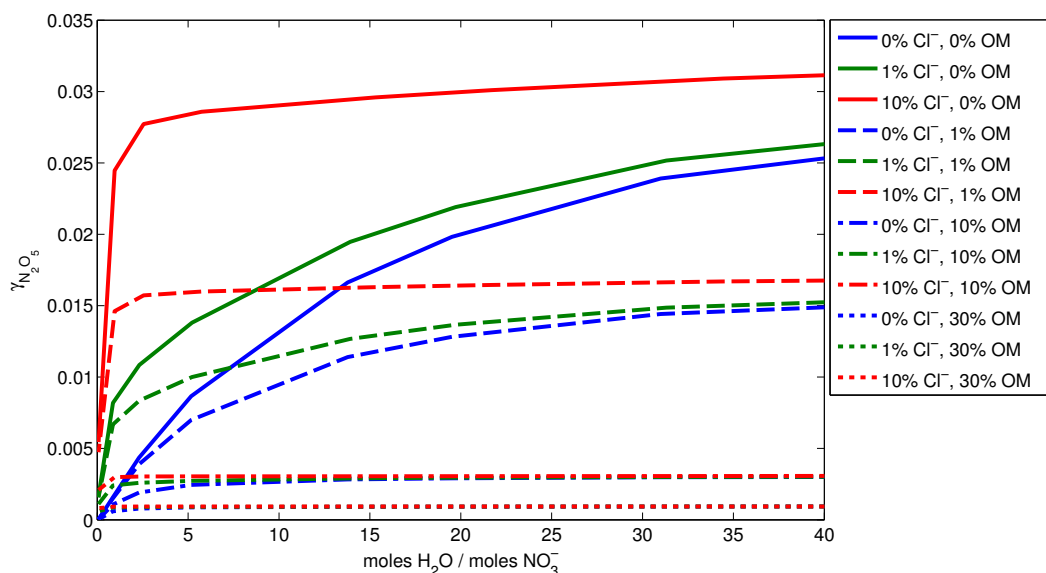


Figure 2: The composition dependence of $\gamma_{N_2O_5}$ for a 1 μm diameter particle, using the inorganic parameterization of Bertram and Thornton (2009) combined with the organic coating parameterization of Riemer et al (2009). For a range of $\text{H}_2\text{O}:\text{NO}_3^-$ mole ratios, the $\gamma_{N_2O_5}$ for totally inorganic particles with a mole content of chloride ions of 0%, 1%, and 10%, are represented by the solid blue, green and red lines, respectively. The suppression of $\gamma_{N_2O_5}$ for these different inorganic particle compositions by an organic shell comprising 1%, 10%, and 30% of the total particle mass are indicated by the dashed, dash-dotted, and dotted lines, respectively.

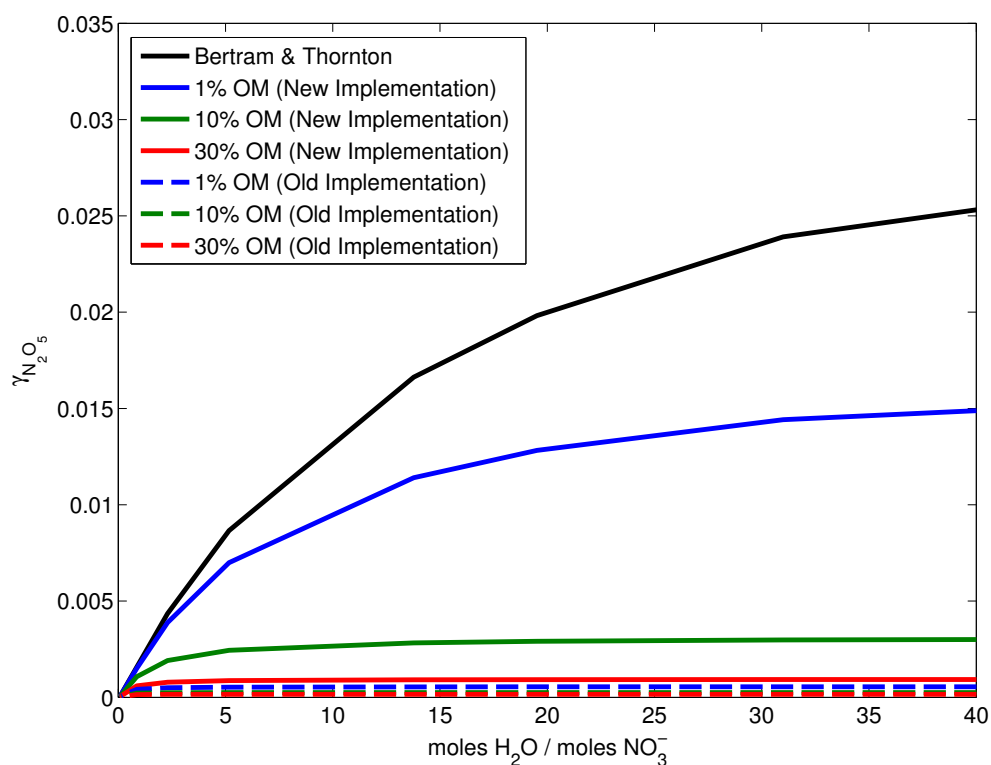


Figure 3: Comparison of $\gamma_{\text{N}_2\text{O}_5}$ when using the old and new organic suppression implementations. The black line indicates the uptake coefficient calculated following Bertram and Thornton (2009), without any chloride ions, for a range of $\text{H}_2\text{O}:\text{NO}_3^-$ mole ratios. For a given particle diameter of $1 \mu\text{m}$ the blue, green, and red lines indicate the uptake coefficient for particles with an organic shell comprising 1%, 10%, and 30% of the total particle mass, respectively. Solid lines indicate the uptake coefficient calculated with the new implementation (consistent with the parameterisation of Riemer et al, 2009), and the dashed lines indicate the uptake coefficient calculated with the old implementation.

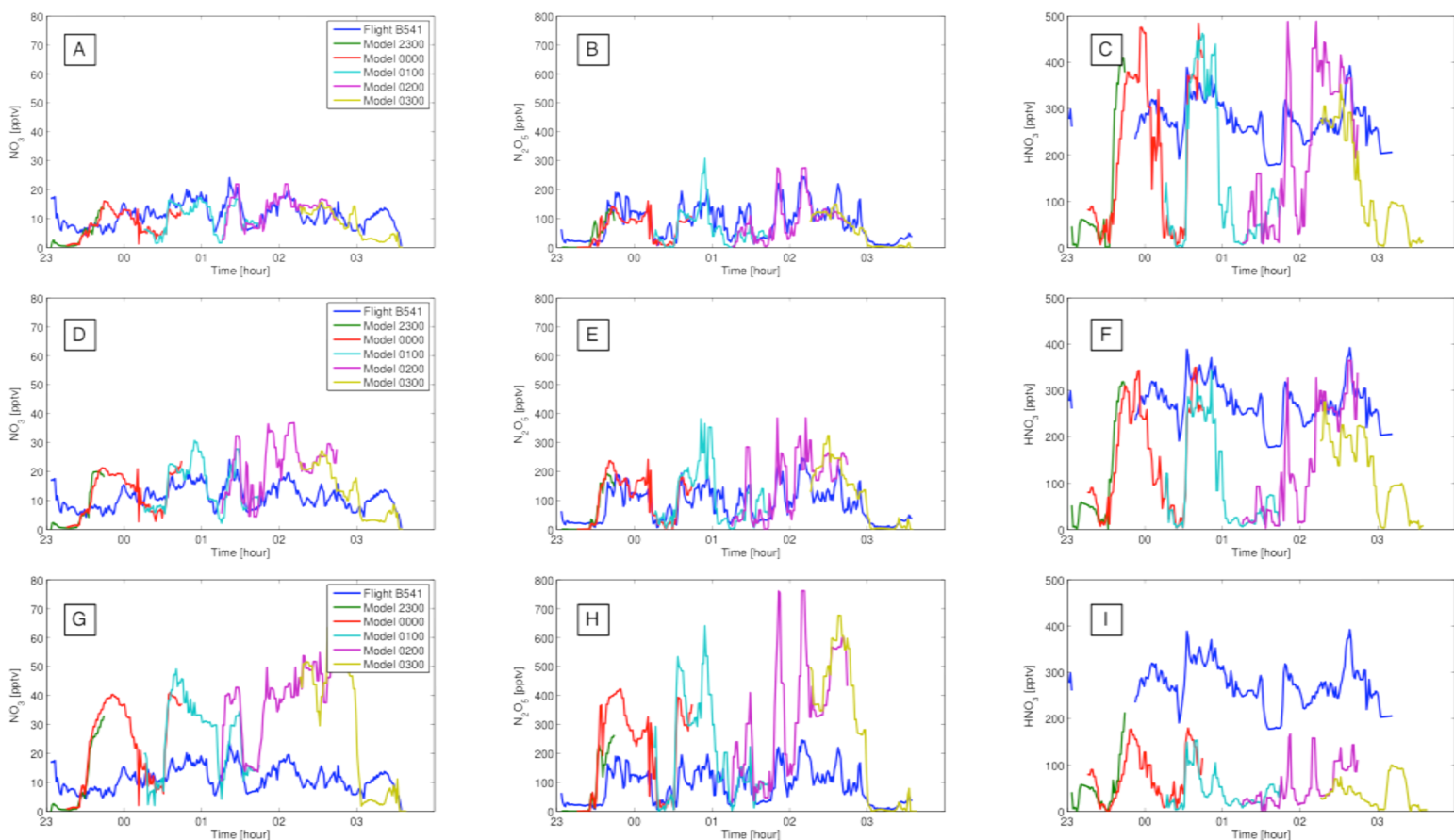


Figure 4: Flight-track measurement-model comparison during flight B541 for NO_3 (panels A, D, and G), N_2O_5 (panels B, E, and H), and HNO_3 (panels C, F, and I). Plots show 1 min averaged measurements (blue lines), and data from the “het on” (panels A-C), “organic suppression” (panels D-F), and “het off” (panels G-I) model scenarios (multicoloured lines).