Interactive comment on “Reactive uptake of N2O5 to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations” by C. J. Gaston et al.

Anonymous Referee #1

This is an interesting manuscript which systematisizes the effects of different organic (mixture)(s) on the uptake of N2O5 on atmospheric particles, relative to an inorganic reference state. The manuscript takes into account organic fraction, organic composition (O/C) and particles morphology (phase separation). Application of an analytical solution of the reacto-diffuse equation considering coatings (Antilla model) with modifications / constraints derived from measurments and adjusting the free parameters gives insights into sensitivity and critical parameters. The authors derrive from the lab results and model a range of possible effects of organic aerosol components for a range of atmospheric conditions and atmospheric organic particle properties. This is showing despite the wide variety of conditions and properties of moxed organic/inorganic particles that reduction of N2O5 uptake is significant and should be considered. The manuscript is well writen, clear, and good to read and can be published as it is. However, the author may consider a few points:

Reviewer responses are numbered and in black. Author responses in red.

1. I would move Figure 1S from the supplement to the manuscript. I like to see the experimental setup when dercibed in the text.

The figure has been moved as requested.

2. Is it possible to plot the Seatlle field data into Figure 8, using the composition and conditions of the individual data points? Would the position and the spread of the Seattle data points tell something about the likely morphology/composition of the particles, which could be verified by other accompanying measurements

Figure 8 (now Figure 9) shows the impact of organic coatings as a function of relative humidity for different types of organics. Because the range in RH sampled by the Seattle data is small and organic mass fractions spanned a different regime from the laboratory experiments, this data couldn’t be represented in Figure 9. However, as shown in the manuscript, mixtures of ammonium bisulfate and polyethylene glycol were found to generally represent N_2O_5 uptake on ambient aerosol, which is why we showed the impact of coatings of PEG as a function of relative humidity.

3. p. 32057, line 19-21: This sentence is difficult to understand. Could you try to reformulate or extent a little what you refer to.

The sentence has been clarified.

4. p. 32069, line 10ff and Figure 6: Any specific suggestions which could explain the lower N2O5 uptake for the two data points. I guess that experimental artefacts can be ruled out ? (e.g. were they taken in the same period or were other measurements in between? Were they taken with the same setup ? You mentioned the exchange of similar equipment.)

Experimental artifacts can be ruled out for the two outlier points since measurements with ABS and other organic compounds with high O:C ratios that showed expected behavior (e.g., ABS and malonic acid) were also made during the same period and with the same equipment. As mentioned in the high O:C section (3.3), we hypothesize that citric acid and glucose are responsible for the observed behavior since both compounds are capable of forming amorphous phases. It is possible they precipitated from the solution.

Typos:

5. p. 32064, line 5: ": : :a similar finding to Antilla et al. (2006)". Turn words to ": : :a finding similar to Antilla et al. (2006)" ??!

The sentence has been modified as suggested.

6. Figure 1: legend inside Figure misplaced

The legend has been moved to the top of the figure.

Interactive comment on "Reactive uptake of N2O5 to internally mixed inorganic and organic particles: the role of organic carbon oxidation state and inferred organic phase separations"
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Anonymous Referee #2
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The authors have systematically investigated the validity of the Anttila (2006) model for predicting the reduction of N2O5 uptake to ammonium bisulfate caused by organic components. They have tuned the model to the results of new experimental datasets by adjusting the rate coefficient of N2O5 reaction and its diffusion rate coefficient in the organic phase, as well as a scaling factor for relative solubility/diffusion in the organic layer and aqueous core. Finally they make predictions for the suppression of the uptake coefficient of N2O5 for various O:C ratios and organic mass fractions in atmospheric particles. The presence of certain organics (low O:C ratio) significantly changes the response of N2O5 uptake to changes in RH. This is an interesting study, which advances or knowledge of N2O5 heterogeneous kinetics in the troposphere and may in the future lead to an improved approach to modeling this very important parameter. The authors may wish to consider the following points in revising their manuscript.

1. Please reduce the unnecessary use of acronyms. Ammonium bisulfate has a chemical formula not much longer than the acronym ABS. Also the structural formula of PEG should be given at one point.

"ABS" has been replaced with "ammonium bisulfate" throughout the manuscript. The structural formula for PEG is now reported in the manuscript.

2. P32059 L5. The surface areas are derived from mobility diameters. Please state the accuracy of the areas thus derived.

The ability of the mobility diameter to accurately represent the actual particle diameter mainly depends on the shape factor of the particle. Because the aerosol particles generated in this study were mixtures of ammonium bisulfate, the particles are assumed to contain high liquid water contents and therefore to be spherical. Shape factors for spherical particles are unity and thus we expect the mobility diameter accurately describes the true particle diameter in this case.

3. P32059 L24. Laminar flow. Please give the Re number.

The Reynolds number is now stated in the manuscript.

4. P32060 Eq1. This assumes exponential dependence between "top" and "bottom". Was this observed ? What was the fractional loss of N2O5 ? Please show raw data, at the very least as supporting information if not in the manuscript.

Figure S1 has been added to the supporting information of this manuscript showing decays of N_2O_5 as a function of injector position in the presence and absence of ammonium bisulfate particles. Both decays show linear behavior on a log scale indicating an exponential dependence on the N_2O_5 signal when the injector is at the top and bottom of the aerosol flow tube. The fractional loss of N_2O_5 was approximately 80%.

5. P32061 L5. Please list the corresponding RH values for each uptake coefficient.

The RH values are now listed for each uptake coefficient.

6. P32062 L24. Please move the description of F to the manuscript. The reader should have optimal access to important features of the data analysis.

The equation for parameter F is now in the manuscript.

7. P32065 L22. This observation(s)

The word "observations" has been changed to "observation".

8. P32065 L28. : : :possibilities exist for why: : :. There are several possible ways to explain why..?

The sentence has been reworded as suggested.

9. P32072 L5: : :potentially: : :..

"Potential" has been changed to "potentially".

10. The dataset presented in Figure 7 looks convincing, with 1:1 agreement. However, if I have correctly understood the procedure used, this agreement has been achieved by the tuning of the model parameters such as korg for each individual condition. The model does not, a priori, predict these uptake coefficients. Perhaps the use of the word predict in the y-axis is inappropriate here. The authors should clarify this.

The reviewer is correct in his/her assessment that the model requires tuning for each condition and does not a priori predict uptake coefficients. We have, therefore, changed the word "predicted" to "parameterized" in Figure 7 (now Figure 8) of the manuscript.

Changes Made to Manuscript:

1. "Ammonium bisulfate" was substituted for "ABS" throughout the text of the manuscript, in Tables 1 and 2, and in Figures 2-6, 8-9.
2. Lines 110-112 clarify standard decays and particle modulation techniques for determining uptake kinetics: "Both standard decays of N_2O_5 as a function of interaction time by moving the position of the injector containing N_2O_5 and modulation of particle concentration at constant interaction time by turning the aerosol flow on and off."
3. Line 128 gives the chemical formula of polyethylene glycol ($H(OCH_2CH_2)_nOH$).
4. Lines 164-165 gives the Reynold's numbers calculated for each flow tube (106 for the 3 cm diameter flow tube and 53 for the 6 cm diameter flow tube).
5. Lines 175-176 reference a new figure (Figure S1) found within the Supporting Information showing a full decay for ammonium bisulfate.
6. Figures 192-193 clarify the corresponding relative humidity values for each reactive uptake coefficient determined for pure PEG particles.
7. Below is main equation used to parameterize the reactive uptake coefficient:
   $$\frac{1}{\gamma} = \frac{\omega R_p}{4D_{gas}} + \frac{1}{\alpha} + \frac{\omega R_p}{4RTH_{org}D_{org}(q_{org}F - 1)}$$
   Lines 236-238 add an additional equation to the manuscript that helps clarify the main equation used in the parameterization:
   $$F = \frac{\coth(q_{org}) + h(q_{aq,}q^*_{org})}{1 + \coth(\mathrm{q_{aq}})\,\mathrm{h}(\mathrm{q_{aq,}}\mathrm{q^*_{org}})}$$
8. Figure S1 from the Supporting Information is now Figure 1 in the main manuscript.
9. Line 478: "potential" was changed to "potentially".
10. The legend for Figure 2 has been placed outside the figure.
11. A legend was added to Figure 8.