Atmos. Chem. Phys. Discuss., 14, C8792–C8802, 2014
www.atmos-chem-phys-discuss.net/14/C8792/2014/

Atmospheric Chemistry and Physics Discussions
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Interactive comment on "Influence of aerosol chemical composition on N2O5 uptake: airborne regional measurements in North-Western Europe" *by* W. T. Morgan et al.

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Received and published: 5 November 2014

We thank the referee's for their comments which will enhance the clarity of our analysis and our discussion of the scientific findings. Each comment is addressed below, with the referee comments highlighted in bold text.

Anonymous Referee 1 Comments

1. Equilibrium of NO3 and N2O5: The authors use a box model to check if the equilibrium is established. Why do you not use directly the actual measurements of NO2, NO3 and N2O5 in a similar fashion to Brown et al. (2003) (see their figure

6)?

The box model is used to test when the assumption of steady-state is established, and as noted in the manuscript and following Brown et al. (2003b), a valid steady-state implies that the system is at equilibrium. This is the standard approach established in the previous literature. We did also perform a similar analysis to that suggested by the referee, which showed good agreement between the calculated and measured equilibrium constants but did not include this in the original manuscript or supplementary material. We will include the comparison as an additional figure in the supplementary material.

2. Aerosol surface area calculation: What hygroscopicity was assumed for the organic material (p. 19683, line 20)?

We assumed that the hygroscopicity of the organic material could be represented by that of fulvic acid, given our inspection of the organic mass spectra. For reference, ADDEM estimates that a 200nm fulvic acid aerosol particle at 85% relative humidity would have a growth factor of 1.10. We will include this as an example in the revised manuscript.

3. Calculating kN2O5: It is not clear from the description how the data was chosen that goes into each fit. This seems crucial for the result. On page 19687, line 20 the authors say: "Case studies were selected during portions of the flight when the aircraft was sampling relatively homogeneous pollution conditions at a constant altitude below 1500m…". Can you justify the data selection more quantitatively? Following Brown et al. (2006), the data is separated into regions with distinctly different chemical regimes. A figure similar to Figure 3 in Brown et al. (2006) would clarify this question.

The case studies were based on individual Straight and Level Runs (SLRs) performed by the aircraft during each flight. These SLRs are typically 5-20 minutes long and this relatively short duration typically means that the pollution conditions are relatively homogeneous i.e. fairly constant aerosol concentrations and composition. Unlike the Brown et al. (2006) analysis, we did not typically observe large changes in aerosol composition over a single SLR as the regional extent of the SLRs was much more limited in comparison. The only instances where large composition changes were observed was when sampling discrete point sources (ships and power plant plume) but these were encountered infrequently and were not representative of the general regional aerosol burden. Such instances were omitted from the analysis as such plume interceptions by the aircraft were short in duration. We will include a brief description and an example figure in the supplementary material to illustrate the data selection process.

4. Calculating gamma values: page 19687, line 6: How was the uncertainty of 36% derived for gamma?

Using the uncertainty values listed in Table 2 of the manuscript, the uncertainty for gamma was calculated via summing in quadrature (the uncertainty is dominated by the SMPS surface area calculation). We will add a note in the revised manuscript to make this clearer.

5. Internal mixture assumption: I wonder how appropriate the assumption is that the aerosol is "internally mixed". This assumption plays into the calculation of the aerosol surface area, but also into the calculation of gamma for the population. I agree with the authors that aerosol away from near-field sources appears internally mixed with respect to hygroscopic properties. However single-particle measurements also show that there can be considerable variability in terms of composition. For example, what if the organic material is not evenly distributed over all particles in the population? Wouldn't this lead to a larger spread of gamma values from the parameterizations (e.g. Fig. 6)?

The referee is correct in saying that a variation in composition across a particle population would produce a distribution of gamma values, though it is not expected that

the gamma value that represents the average particle composition is greatly different to the average of the gamma values across the particle population. A full examination of this is beyond the present work as we have no constraint from measurements.

6. Figure 5: Given that there is essentially no relationship between gamma and the organic mass fraction, is there any reason to believe that the organics are mostly water soluble (i.e. they don't form a distinct coating)?

The lack of a relationship with organic mass fraction is both puzzling and interesting given previous observations in both the laboratory and ambient studies showing a clear reduction in uptake due to the presence of organics. As we noted in the discussion, organic aerosol is ubiquitous in our study and contributes a relatively narrow range with respect to its mass fraction compared to sulphate and nitrate. Consequently, there could be a broad suppressive effect but little dependence on further organic aerosol enhancements. As the referee suggests, the assumption of a distinct organic coating may be erroneous but we do not have measurements in this study to constrain this. The parameterisations including organics are based on this coating assumption (aside from the Evans and Jacob parameterisation) but if the organics are predominantly water soluble, this would potentially explain the poor performance of these parameterisations compared with the gamma values calculated from the steady-state method. We will add this point to our discussion of the organic influence on uptake in the revised manuscript.

A further paper is planned that will explore the role of organics by combining measurements with model results but this is beyond the scope of this current paper.

Typographical errors and other minor comments:

p. 19680, line 16: What is SLR?

Straight-and-Level Run. We will add this to the revised manuscript.

p. 19682, line 1: should read "system has to be in steady-state"

Corrected in revised manuscript.

p. 19686, line 21: "planetary boundary layer". Should read residual layer.

Changed in revised manuscript.

p. 19687, line 14: the term "gradients" is wrong here. Please rephrase.

Comment relates to p. 19686 rather than p. 19687. We will omit "gradients" from the revised manuscript and rephrase the sentence.

Figure 3: Explain in the caption what the boxes, error bars etc. are.

Added to revised manuscript.

Figure 6: Some axes labels are missing.

This is a stylistic choice to avoid cluttering the figure with unnecessary labels as the scales used are the same in every panel i.e. the y-axis represents the parameterisation and the x-axis represents the steady-state method in each panel. We will add a note to the figure caption to make this clearer in the revised manuscript.

Anonymous Referee 2 Comments

1) It is my understanding that when determining if the steady-state calculation is correct, a model is often used to assess the time required to achieve SS. This model should include the loss rate of nitrate radicals to various VOCs. Was this done? And if so, what measurements were used to assess this and more generally, what is the relative strength of NO3 reactivity compared with N2O5 reactivity in these air masses? It is important to highlight this comparison given that the data (as shown in Fig. 4) appears to hold some of these answers.

The referee is correct. The model includes the loss rate of nitrate radicals to various VOCs. We neglected to mention the gas-phase scheme used in the model and will include details of this in the revised manuscript. The box model used is a modi-

fied version of the Lowe et al. (2009) model, where the gas-phase chemistry scheme has been replaced with the CRIv2-R5 chemistry scheme (Watson et al, 2008). This includes many reactions between the nitrate radical and VOCs, and is the same chemistry scheme as that used for the regional modelling studies conducted by Lowe et al. (2014). The scheme is validated against the Master Chemical Mechanism (MCM, Jenkin et al., 2003), while the performance of the scheme on the regional scale has been assessed in Archer-Nicholls et al. (2014).

The focus of this study is on the chemical composition controls on N2O5 uptake, rather than assessing the relative contribution of different pathways for loss of NO3 and N2O5. For context, we will add a discussion to the manuscript citing Stone et al. (2014) who assessed this using a measurement-constrained box model and found that heterogeneous uptake dominated (66%) the loss of NO3x (N2O5+NO3) during the summer night-time during RONOCO, with the NO3+VOC pathway accounting for 7%.

2) In equation E3, what surface area was used? An average surface are for the entire flight? An average over the flight leg used to generate the lines in Figure 2? Given that NO2 (and thus Keq[NO2]) often co-vary with surface area, it would be important to note how the variability in the surface area impacts this calculation.

The surface area was calculated for each SLR used for the analysis. The variability that this introduces to the calculation of gamma is illustrated by the bars in Figure 6, which shows the standard deviation in gamma for each SLR. This variation is due to changes in aerosol surface area concentration over a given SLR. We will add a note to the manuscript clarifying this.

3) In section 2.4 the authors describe how the ambient surface area was determined using a calculation of the hygroscopicity. It would be helpful to include the values that were used. It appears that the authors used a very small growth factor (similar to fulvic acid). What is the sensitivity of the conclusions to this

decision? Given that the retrieved uptake coefficients are already close to the upper limit observed in the laboratory for tropospheric mimics (0.03) a more hygroscopic organic fraction would act to increase the particle surface area and thus decrease the retrieved gamma value.

We will include representative values for the hygroscopicity in the revised manuscript in a similar manner to the quoted values for fulvic acid in response to referee 1's comment 2.

As we do not have hygroscopicity measurements to determine the actual growth factor of organics, we used a typical analogue for organic aerosol which has similar chemical functionalities to our aged aerosol based on the measured mass spectral profile. For the sake of comparison, we can test the sensitivity to this by increasing the growth factor for organics using a representative value from the literature; Gysel et al. (2007) estimated that the growth factor for organics at 90% RH was 1.2 based on HTDMA measurements in the eastern UK region, which should be relevant to our study here. Increasing the organic growth factor in the ambient surface area calculation by 10% to account for this difference causes gamma to decrease by approximately 5% averaged across the dataset (inorganics are a major fraction of the aerosol so the impact of an increased organic growth factor is reduced). Such an impact is minor, particularly when accounting for the uncertainties inherent in the analysis. We will add this as a discussion point to the revised manuscript.

4) Again, with respect to hygroscopicity. How were the organics treated in calculating particulate water content for the Bertram and Thornton parameterization? Were they also treated as fulvic acid? How might this decision impact the resulting conclusions?

The organics were treated in the same way as for the growth factor calculation so that the calculations were consistent. Increasing the organic hygroscopicity increases the water content, which increases the gamma from the Bertram and Thornton parameterisation by approximately 6% averaged across the dataset. This will lead to a further overestimation by the parameterisation, which is compounded by the reduction in the steady-state calculated gamma value. Again, this impact is minor compared with the stated uncertainties. We will add this as a discussion point to the revised manuscript.

5) The correlation of gamma N2O5 with NO3 as shown in Fig. 5 is not very strong and appears to be guided by two points. What does it look like as a function of [NO3-]/[H2O]l?

Excluding the two points referred to by the referee reduces the r-squared value to 0.21. Plotting gamma as a function of the H2O:NO3- molar ratio following Bertram and Thornton shows a general increase in gamma with the ratio, that broadly follows the parameterisation although with some deviation from this and a general over-prediction by the parameterisation (as expected based on the scatter plots in Fig. 6). For reference, the r-squared is 0.45, although this relationship is not expected to be linear. We will add this plot to Fig. 5 as an additional panel and discuss it in the revised manuscript.

6) One of the more interesting aspects of this work is that there does not appear to be a strong correlation between gamma N2O5 and organics as has been shown previously. Given that the data set appears to be quite robust and a high resolution AMS was on the airplane, it would be of interest to push this question a bit further. In figure 5, a correlation against the organic mass fraction is shown. Is it possible to expand upon this and look at a correlation with O:C for particles that have similar [NO3-]/[H2O]l? This would help shed more light on the role of the organic fraction in suppressing N2O5 uptake.

The AMS on the aircraft was a compact-time-of-flight version of the instrument, not the high-resolution version as stated by the referee. As such, the O:C ratio can only be estimated, rather than directly measured.

Before addressing the referee's comment, we note that in the ACPD version of the manuscript, the O:C was calculated using the equation provided by Aiken et al. (2008), which relies on the signal intensity of the organic peak at m/z 44. As noted in the manuscript, this yielded a narrow range of O:C from 0.43-0.58. Subsequent to our submission, Canagaratna et al. (2014) have a manuscript in ACPD which shows that the Aiken et al. estimation is biased low by 27%. Consequently, we will revise our quoted O:C range upwards in the revised manuscript following the calculation in Canagaratna et al. (2014).

Regarding the referee's comment, the range in O:C in our study is rather narrow and subject to significant uncertainty given that it is estimated rather than directly measured. Inspection of the data as the referee suggests yields no obvious relationship between gamma, [NO3-]/[H2O]l and O:C. We will add a comment on this point to the revised manuscript.

7) What diffusion constant for N2O5 in the organic coating was applied for E6?

We followed the method described in Riemer et al. (2009), which follows the analysis described in Anttila et al. (2006), for the calculation of the diffusion constant for the organic coating. They showed that HorgDorg is approximately 0.03HaqDaq for organic coatings consisting of condensed monoterpene oxidation prodcuts. Haq is the Henry's law constant for N2O5 for the aqueous phase (5000 M/atm) and Daq is the diffusion coefficient of N2O5 in the aqueous phase (10-9 m2/s). We will add these details to the revised manuscript.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 19673, 2014.