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Widening the gap between measurement and modelling of secondary organic aerosol properties?

N. Good[1], D. O. Topping[1,2], J. Duplissy[3,], M. Gysel[3], N. K. Meyer[4,*], A. Metzger[3], S. F. Turner[1,***], U. Baltensperger[3], Z. Ristovski[4], E. Weingartner[3], H. Coe[1], and G. McFiggans[1]**

[1]School of Earth Atmospheric and Environmental Sciences, University of Manchester, Manchester, M13 9PL, UK
[2]National Centre for Atmospheric Sciences, University of Manchester, Manchester, M13 9PL, UK
[3]Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, 5232 Villigen, Switzerland
[4]ILAQH, Queensland University of Technology, P.O. Box 4233, Brisbane QLD, 4001, Australia
[*]now at: Laboratory for Energy Systems Analysis, Paul Scherrer Institut, 5232 Villigen, Switzerland
[**]now at: Department of Physics, Centre Européen de la Recherche Nucléaire, 1211 Geneva, Switzerland
[***]now at: Experimental Solid State Physics Group, Blackett Laboratory, Imperial College London, SW7 2BW, UK

Correspondence to: G. McFiggans
(g.mcfiggans@manchester.ac.uk)

1 Introduction

The supplementary material aims to quantify the uncertainty associated with the measured growth factors ($GF_{D0,RH}$) and critical supersaturations (S_c) in the context of the models and model sensitivities presented in the manuscript. The measurement uncertainty is shown in Figure 3 of the original manuscript. The uncertainty in the measured growth factor occurs mainly as a result of the finite ability to accurately and precisely control and and measure the flow, voltage and relative humidity (RH) applied to the DMAs (Massling et al., 1999) as well as the finite resolution of the DMA's transfer functions (Cubison et al., 2005; Gysel et al., 2009). When operated un-humidified the uncertainty of the growth factor measured by a TDMA is ~ $\pm$ 0.02. Humidifying the system increases the uncertainty depending on the accuracy and precision of the RH measurement and temperature control of the DMA (Duplissy et al., 2009). The uncertainty of the measured $S_c(D_0)$ presented in the paper is most significantly due to the ability of the operator to set adequate supersaturations in the CCN counter to constrain the critical point. Only when the properties of the sample aerosol remained constant did the precision/repeatability of the CCN counter's supersaturation settings limit the measurements.

The κ values calculated from the CCN counter's data (κ_{CCN}) measured simultaneously to the growth factor humidograms after approximately 8 hours of photo-oxidation were ~0.1. It was from this period that the ADDEM water activity parameterisation was derived, as described in the main text. The range of κ values predicted from the uncertainty in the measured S_c during this period was used to represent the range of supersaturations. The range of S_c predicted using the κ-model from the uncertainty in the measured values is illustrated in Supplementary Figures 1-3 (shaded red to blue). The range of κ values calculated from the uncertainty in each HTMDA's measured growth factor at 90%RH (κ_{HTDMA}) are shown in Figures 1-3 (shaded red to brown) for each instrument.

2 Supplementary Figure 1 - H_{MAN}'s measurement sensitivity to κ

Supplementary Figure 1 shows the sensitivity to the measurement uncertainty in κ for H_{MAN} as described in the introduction. The range of κ as a function of RH (yellow symbols) is within the range of uncertainty in $\kappa_{H_{MAN}}$ at 90% RH. ADDEM predictions including the effect of bulk to surface partitioning (pink symbols) also fall just above the upper limit of the measured S_c values. The ADDEM predictions assuming the surface tension of water (red symbols) are above the range of S_c predicted from the HTDMA. The sensitivity of the ADDEM predictions assuming the surface tension of water to varying the molecular weight (red crosses) and the density (red squares) over the realistic range is small compared to any of the fundamental changes in the model. ADDEM incorporating the parameterised proxy for organic aerosol surface tension (green symbols), results in S_c lower than the range of S_c predicted from $\kappa_{H_{MAN}}$. Again the sensitivity to varying molecular weight (200-500gmol^{-1}) and density (1200-1800kgm^{-3}) (green crosses and squares respectively) is relatively small compared to more fundamental changes in the models. The ADDEM predictions with the proxy surface tension tend towards the measured values with increasing D_0.

3 Supplementary Figure 2 - H_{QUT}'s measurement sensitivity to κ

The data from H_{QUT} (shown in Figure 2) for the ADDEM partitioning case (pink symbols) gives S_c at or slightly above the upper limit of the measured S_c's uncertainty. ADDEM including organic surface tension proxy (green symbols) gives S_cs which tend to the measured values at higher D_0. The difference between The κ_{HTDMA} and κ_{CCN} derived S_c is even larger than for H_{MAN}. The κ_{HTDMA} and ADDEM predictions assuming the surface tension of water significantly over-predict S_c.

4 Supplementary Figure 3 - H_{PSI}'s measurement sensitivity to κ.

For H_{PSI} the range of S_c derived from $\kappa_{H_{PSI}}$ as a result of the uncertainty in $GF_{D0,RH}$ lies within the range of S_c derived from κ_{CCN} (the dashed black line indicates the lower limit of S_c derived from κ_{CCN} which are otherwise obscured by the HTDMA derived values). The ADDEM prediction incorporating partitioning (pink symbols) fall within or just above the upper limit of the measured S_c's uncertainty. The ADDEM predictions assuming the surface tension is that water predict S_c slightly below the measured values. The ADDEM predictions incorporating the surface tension proxy (green symbols) are below the measurements and their uncertainty.

5 Conclusions

Based on the uncertainties presented, the model predictions derived from each HTDMA and their consistency with the CCN measurements generally fall into distinct agreement and disagreement depending on the formulation. For H_{MAN}, H_{PSI} and H_{QUT} the ADDEM predictions incorporating the surface tension proxy are on or around the upper limit of the measured S_c's uncertainty. For H_{PSI} the κ-model using κ_{HTDMA} gives good agreement, whilst for H_{QUT} and H_{MAN} it is over-predicted. There is a trend of κ increasing with RH for each HTDMA, however this is also within the uncertainty of the κ value at 90$\%$RH, even for H_{QUT} which shows the largest variability. The ADDEM predictions assuming the surface tension is that of water do not give agreement using the a_w derived from any of the HTDMAs. ADDEM incorporating the organic surface tension proxy converges on the measured S_c at larger diameters for H_{MAN} and H_{QUT}, it under-predicts S_c for H_{PSI}.

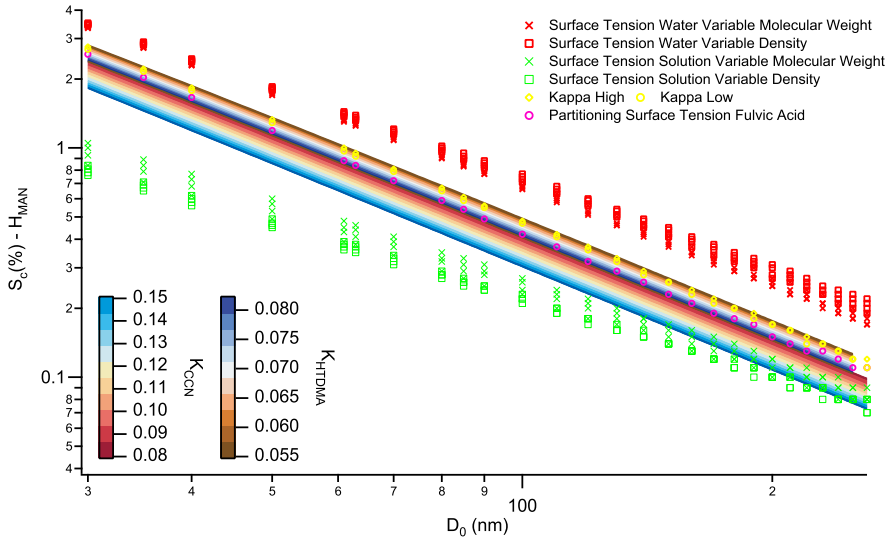

Fig. 1. H_{MAN}: sensitivity of the κ predictions to the measurement uncertainty.

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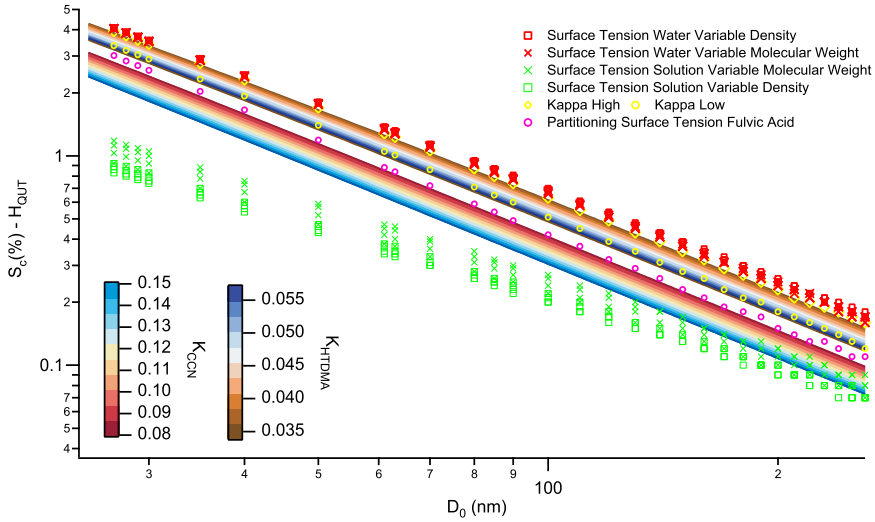

Fig. 2. H_{QUT}: sensitivity of the κ predictions to the measurement uncertainty.

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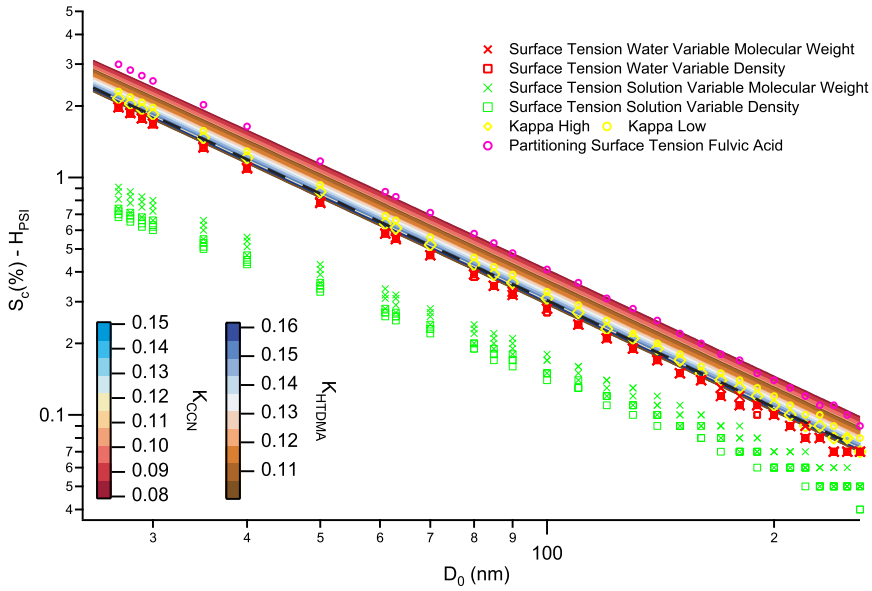

Fig. 3. H_{PSI}: sensitivity of the κ predictions to the measurement uncertainty. An additional black dashed line is shown in this figure to indicate the edge of the K_{CCN} sensitivity hidden by the K_{HTDMA}.