

## ***Interactive comment on* “The effect of physical and chemical aerosol properties on warm cloud droplet activation” by G. McFiggans et al.**

**G. McFiggans et al.**

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The authors would like to thank Dr Leitch for the huge effort which must have been put in to his in-depth review and for his constructive criticism.

The observation that the paper is "a connection of pieces written by a large number of authors" is correct to some extent. Although attention was paid to ensure consistency of writing style and suppression of excess verbosity, we recognise that some improvement was possible and the manuscript has been revisited to address these concerns.

We are largely, but not wholly, in agreement with Dr Leitch's summary of the paper:

"This is not a comprehensive review, in so much as it deals with more recent advances, but it is authoritative. The most recent work included tends to be a little parochial, and

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I think it is important that the authors draw a line for “published” work to be included in this paper, e.g. revise the paper to include anything that has been published or accepted for publication before an appropriate date in 2005. Most importantly, this should not be a forum for unpublished work (further comments about this are below). There are also a few technical issues (see my specific comments). My overall impression is positive, and with some revision this could be an excellent summary."

Indeed, the paper is not intended to be a comprehensive review, but should serve as an authoritative summary. We have revised the citations to reflect the status of the recent articles and, with very few exceptions, only refer to published or accepted articles. The very few exceptions are clearly stated as such and are retained because of high potential importance to the relevant fields. With regard to new unpublished research within the manuscript, there are several important new aspects that the paper brings to the field. By their inclusion, we open them up to review and, expecting the description of these new findings to be self-contained, invite the scrutiny of the reviewer. As we believe is fitting for a paper that is both a research and review paper, new data from the authors are included but they are only from techniques, such as the AMS, that are already described in the literature. We have modified the script to ensure that unpublished work is fully described. We do not agree that a research paper "should not be a forum for unpublished work".

Responses to specific comments:

Page 1, Ou and Liou study noted and referenced

Page 2, We are in agreement that the section in the introduction could be read in a manner that understates the importance of any dynamical effect on droplet number. An additional sentence has been added to alleviate the confusion:

"Should all dynamical considerations remain relatively constant, such observations can be used to derive relationships between the aerosol distribution and cloud distribution properties."

Page 2, Dr Leaitch raises an interesting point about whether it is the dynamical complexity or that of the aerosol composition that precludes a realistic treatment of cloud formation. A main contention of the paper is that, without a consideration of the complexity of the aerosol, it is impossible to conduct a realistic sensitivity study to resolve this question. Efforts such as that presented in Table 1 demonstrate that a simplified treatment of the complexity may lead to the conclusion that the composition plays a minor role in droplet number. Section 4 details why such a treatment is too simplified and the possible additional effects that composition may have. We believe that the discussion as presented in the manuscript is balanced and that, since the paper focusses on the aerosol properties, the emphasis on dynamical aspects need not be increased. In addition, we believe that the statement is clear and that the part quote made in the comment is taken out of context; the comment in the manuscript only referring to the effect of solubility "this evidence suggests that the effect of limited component solubility on droplet number is unlikely to be significant".

Page 2, It is not claimed in the sentence "Long-range transport... are not always free from anthropogenic influence..." that this is the only way that pollution affects remote regions, but it illustrates a mechanism that ensures that remote regions are affected by pollution.

Page 2, "rich" and "level of" have been removed from the offending sentence

Page 2, "the" has been added to the offending sentence

Page 3, "\nu" replaces "i" and the definition of "\nu" has been made

Page 3, the offending adjectives have been removed

Page 3, Equation 6 has been corrected

Page 4, The paragraph has been rewritten to minimise the confusion. We concur with the Dr Leaitch that the clarity was less than perfect. The revised paragraph reads:

"For any given composition and supersaturation (which, around cloud base, is directly

proportional to updraught velocity), whether a particle activates is solely dependent on its dry size. At constant updraught velocity, a distribution of such particles of varying sizes will activate if their corresponding critical radius is reached. As more particles activate and grow, they will compete for available water vapour. The water supersaturation will continue to rise above cloud base but will slow as growing droplets scavenge the water vapour and relatively fewer additional (smaller) aerosol particles will activate. When supersaturation sources and sinks balance, the peak supersaturation is reached - usually within a few 10 s of metres above cloud base. Following this point, the growing droplet population will lead to a reduction in supersaturation. No new particles will activate and the most recently activated droplets may evaporate. Some particles will not have sufficient time to reach their critical radius even though their critical supersaturation is reached. This results from water vapour scavenging by the larger droplets reducing supersaturation to below the critical value of the smaller particles before sufficient water vapour can condense (such kinetic limitations are discussed further in section 4). Only particles reaching a certain size will survive and grow. Some of the largest particles may not actually activate, but may be large enough to be considered as droplets since even at their subcritical sizes they will often be greater than 10 or 20 microns in radius, deplete water vapour, and even act as collector drops. A pseudo "steady-state" or quasi-equilibrium is eventually reached for a constant updraught velocity where the decrease in saturation ratio by condensation to the droplet population and the increase in saturation ratio owing to the updraught maintains a broadly constant supersaturation with increasing altitude with the maximum just above cloud base."

Page 5, the limitation of the Twomey parameterisation has been mentioned; it does indeed work well at small  $k$ , /provided  $C$  is  $< \sim 500^*$ / (e.g., Feingold and Heymsfield, JAS 1992, Fig 5).

Page 5, We thank Dr Leitch for his comment here. Noting first that a function is monotonic if its first derivative (which need not be continuous) does not change sign and that a monotonic increase on a loglog plot will still be monotonic on a linear scale,

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we have revised the paragraph to state:

"The Twomey equation, and most others developed to link number of activated droplets to a sub-cloud aerosol concentration (either mass or number), usually assume that the aerosol type is relatively homogeneous. Some parameterizations yield a monotonic increase in cloud droplet concentration (e.g., Boucher and Lohmann, 1995) whereas others show a tendency to saturate (for example Hegg, 1984; Jones et al. 1994). In general they are well approximated by power-law dependences of  $N_d$  on  $N_a$  or the mass concentration of aerosols. The parameterisations of Ghan et al., 1998 and Feingold et al. 2001 exhibit similar behaviour but following saturation, show a decrease in  $N_d$  with further increases with  $N_a$  at very high aerosol concentrations (order  $10,000 \text{ cm}^{-3}$ )."

Page 7, The phrase was mistakenly left in a previous version of the script, but not that which found its way to ACPD. We do not know which version of the manuscript Dr Leitch is commenting on (that it is not the print or web versions from the COSIS website is also evident from the page numbers).

Page 7, Dr Leitch is correct, Table 1 is calculated in our work. In section 3.1.3 p15 line 13 we clearly state "Here we repeat this analysis for sensitivity of drop number concentration  $N_d$ " and on line 16 "for conditions similar to Feingold (2003)". An additional phrase "using the same model" has been added. The range of conditions has been added to the caption.

Page 7, We thank Dr Leitch for the discussion of the results of Table 1. It is true that, when using only varying soluble fraction to represent composition variability, the size distribution parameters are more important as they provide a more direct means of increasing the amount of soluble material. However, in a "constant aerosol mass" framework, this would obviously not be true. When, e.g., we increase  $r-g$ , we clearly increase particle mass and therefore the population-averaged solute term. When we change  $w$ , we have a very direct control over supersaturation supply. The same is true

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of changing Na. Also, Ervens et al. (2005) indicates that composition (as represented by molecular weight, solubility, van't Hoff, and surface tension) are less important than many have stated because of opposing effects on Nd. However, it is clear that composition effects may be much more complex than represented in either Table 1, or Ervens et al. (2005).

We believe the emphasis in Dr Leaitch's comment is too dogmatic. Table 1 does indicate that the strong influence of the first order effects of updraught velocity and total aerosol loading are very significant. It also shows that the sensitivity to insoluble volume fraction, the only composition dependent parameter reported in table 1, is so great as these strong effects as treated in the model. This is not to say that composition does not play a role. The insoluble volume fraction may participate in determining the Raoult term during activation. As treated in the model, it will play no role in the Kelvin term. In addition, such a representation of composition will play no role in potential kinetic limitation of water vapour mass flux. There are possible effects of trace gases, films, interactions and partitioning within the droplet that could be important. The range of composition effects is treated in great detail in section 4. The discussion of such composition effects is therefore much greater than just a few "disclaimers" in section 3.1.3. An emphasis of the paper is on these composition effects. The purpose of Table 1 is to illustrate that such composition effects should be placed in the context of other great sensitivities. That the size distribution and updraught are significant is obvious. The former is well covered by the appropriate section and the latter is not the focus of this work.

Page 7, We thank Dr Leaitch for pointing out the possible confusion here. The modified sentences read:

"It must be remembered that number of activated droplets is dependent on the number distribution of particles of a given type and not directly on the mass loading. Although the activation of an individual particle is dependent on its (soluble) mass, techniques which coarsely probe component distribution loadings by mass will not provide ade-

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quate insight to predict droplet number. Composition is likely to be important only in a limited size range: ..."

Page 8, "The assumption that BC belongS to the insoluble fraction of the aerosol has been questioned by recent experiments" Table 1 indicates that the soluble composition is of relative less importance, and now it is being suggested that BC may be important.

We believe that an oversimplistic interpretation of Table 1 may be responsible for the incorrect emphasis being made in the comment. The insoluble volume fraction, if treated simplistically using equation 6 is indeed relatively unimportant as illustrated in Table 1. Section 4 demonstrates a number of effects that soluble components may have on activation behaviour. If BC is not completely insoluble, it can contribute to such effects which are not considered in Table 1. In addition, if BC is not completely insoluble, water activity relationships and insoluble volume fraction inferred from HTDMA GFD measurements will be affected. This is the significance of the statement.

The phrase "the organic partitioning between water droplets and insoluble material is crucial." has been rephrased:

"an understanding of organic partitioning in cloud droplets (whether dissolved or present as insoluble inclusions) is crucial to our understanding of their possible effects on cloud activation."

Page 9, Again, the typo that Dr Leaitch refers to was legacy from a previous version. This sentence was correct in the ACPD version.

Page 9, We thank Dr Leaitch for the additional reference which we have now included:

Rupakheti, M, W. R. Leaitch, U. Lohmann, K. Hayden, P. Brickell, G. Lu, S. M. Li, D. Toom-Saunry, J. W. Bottenheim, J. R. Brook, R. Vet, J. T. Jayne, D. R. Worsnop, An intensive study of the size and composition of submicron atmospheric aerosols at a rural site in Ontario, Canada, *Aerosol Sci. Technol.*, 2005, 39, 8, 722-736

Page 10, We contend that the sentence is obviously true and very clear. After all, the

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use of "may" rather than "will" ensures that the linkage is not claimed to be ubiquitous or incontrovertible. However, we have appended an explanatory note referring to Figure 7. Although an enhanced aerosol loading and changes in distribution shape resulting from the addition of organic material will lead to increased size distribution parameters cf. Table 2, we do not believe the primary effect of the organics is one of shaping the size distribution; indeed, on an equal mass basis this is undoubtedly true. The discussion is in terms of a "correct" interpretation of aerosol composition for a known distribution:

The high organic content at sizes around the droplet activation threshold suggests that the effect of organics on warm cloud activation may be much larger than their contribution to the overall mass budget of submicron particles. For example, with reference to all panels other than F and H in figure 7, the organic to inorganic ratio below 200 nm dry diameter is clearly higher than the average ratio across the sub-micron distribution. It may be expected that any effect that organic components have on activation properties is exacerbated here. Since particles greater than 200 nm are likely to activate at any reasonable updraught velocity, droplet number is most likely to be influenced by composition effects for the very fine particles below 200 nm in diameter.

Page 10, No discussion of night-time nitrate is made in the paper. The lack of correspondence between the diurnal patterns of nitrate and sulphate (/ organic) modes in the Rupakheti reference suggests that the night-time nitrate enhancement is not via the process discussed in this script (neutralisation of sulphate by ammonia emission leading to nitrate uptake) which does not tend to have a night-time maximum. Hugely elevated night-time nitrate has been observed using the AMS in a number of European field projects, often associated with local or nearby fog events. We're not sure what a discussion of night-time elevated nitrate adds to the current paper.

Page 10, The reference to the unpublished data has been replaced by a reference to section 6.3 where the data are presented for review. In addition, the description of the finding of Bahreini et al. as been modified after correspondence with the authors.

Page 10, The discussion of the mass spectral fingerprints is necessarily brief, but well-referenced. The wording of the paragraph detailing the significance in terms of the oxygenation and attribution to the part of the spectrum where the OOA and HOA material is likely to be found has been verified with authors of the referenced material.

Page 11, The advantages and disadvantages of the respective techniques are well described. Co-authors of the manuscript are very familiar with the instruments and the wording reflects the expertise of the co-authorship. However, to try to strike the balance that Dr Leitch seeks, we have added the following statement to the first paragraph of 3.1.4.2.2:

"However, the single particle techniques are not as quantitative in describing bulk composition as the AMS results described above."

Page 11, The cross-reference has been made.

Page 11, The reason it is hard to prepare extremely pure sulfuric acid particles is probably that organics are ubiquitous on laboratory surfaces such as the interior of DMAs, some of these ubiquitous organics are semi-volatile enough to partition onto particles, and sulfuric acid seems to readily take up small amounts of organics. The converse, sulfate contamination of generated organic particles, is less likely because the common sulfates aren't semi-volatile. There is another corollary that is likely, however. It is probably hard to generate particles of a pure organic substance without them becoming contaminated with small amounts of other, unknown organics.

Page 11, "Consequently, the widespread photo-oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> in the sunlit atmosphere ensures that any particle that has spent much time in the atmosphere has acquired at least a small percentage of sulphate."

This is a qualitative statement that does not need a reference.

Page 13, The statement is a little more subtle than simply stating that smaller, less hygroscopic particles are less likely to activate. The point is that, because the smaller

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particles are less hygroscopic, if an air parcel which would activate, say, 120 nm particles in a given updraught instead encounters an updraught which would activate particles of 75 nm of the same composition, the 75 nm particles would not activate since they are not of the same composition but are less hygroscopic. Hence an even greater updraught would be required to activate the 75 nm particles. This means that there is a smaller sensitivity to updraught velocity than if the particles were of the same hygroscopicity at all sizes.

Page 13, The second half of the sentence says quite a lot about the aerosol mixing state that is not mentioned in the first half.

Page 13, Reference tables 3 and 4, as stated.

Page 13, The sentence has been rewritten:

Only a few of the HTDMA measurements of free tropospheric aerosols unaffected by recent anthropogenic influence taken as part of the Global Atmosphere Watch (GAW) programme at the Izana (Tenerife, 2367m a.s.l.) and Jungfraujoch (Switzerland, 3580m a.s.l.) stations have been published.

Page 13 It is true that the measurements at Izana (Tenerife) cover only ~10 days and hence provide only a snapshot. However, HTDMA measurements at the Jungfraujoch (Switzerland) site have been made in three winter field campaigns of >3 weeks duration each with very similar findings for the hygroscopic growth of aerosol particles. It can hence be stated that the free tropospheric particles encountered at the Jungfraujoch are readily hygroscopic with the exception of mineral dust events as already mentioned in the original text.

Page 14 The measurements reported by Aklilu and Mozurkewich (2004) could not be included in table 3 and 4 (growth factors at 90% RH) since they were made at 80% RH. Carrico et al. (2005) have reported measurements at 90% RH / 100+200 nm dry size for pyrogenic and biogenically influenced aerosols. However, while this manuscript

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illustrates the trends of hygroscopic growth factors of accumulation mode particles under increasing influence of pyrogenic or biogenic influence, typical growth factors under clearly biogenically dominated conditions where not presented separately and also not in a manner matching the format chosen for table 4. Nevertheless both publications provide important information and the findings are included in the discussion of the tables.

Page 14, Cross reference to section 3.2.3 has been added

Page 15, We deliberated for some time on whether to include closure descriptions in section 3, but thought that it made more sense to discuss closure in detail in a section of its own (5). The reason that the closure is discussed after the detailed theory section is that a full consideration of the different levels of closure is better done in the context of these considerations. In contrast, the discussion of CCN measurements does not require this context and is introduced in the composition and properties section 3.

Page 16, This comment, again, refers to an old version of the manuscript. This error never made its way to ACPD.

Page 16, We agree with Dr Leaitch and this has been rephrased:

Investigations planned for a large continuous-flow instrument (Stratmann et al., 2004) may contribute to resolution of this issue.

Page 16, We disagree with Dr Leaitch here. Any linkage between GFD and CCN properties is entirely incidental to Section 3.2.3. Section 3.2.3 is concerned solely with the mixing-state of ambient aerosol inferred from HTDMA measurements. It is a completely distinct way of interpreting the GFD measurements and does not actually use the absolute values of the GFD, but investigates the manner in which components are mixed within a distribution based on the distribution of GFD (GFD breadth, separation etc.). This mixing state (a distribution property) will affect CCN activation in a different way to hygroscopicity (an intrinsic property of individual particles). Hygroscopicity is

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dealt with in section 3.2.1 and mixing-state in 3.2.3.

Page 16, The word "finding" has been replaced by "description" and this is an obvious statement (almost by way of definition), rather than a research finding.

Page 16, A reference to equation 1 has been added: The absolute value of hygroscopicity at a given particle size will determine the critical supersaturation for cloud activation, directly influencing the water activity in equation 1.

Page 17, The effect truly is a suppression of the number of solute molecules, since the concentration of molecules in a discrete surface layer removes the molecules from the bulk solution interior. This is important when the number of molecules in the surface layer is significant compared with the number in the bulk - i.e. for small particles.

Page 18, The sentence has been rephrased: Bilde and Svenningsson (2004) postulated that an increased critical supersaturation was due to an undissolved core forming an "activation barrier" when the growing particle is smaller than the fully dissolved wet size.

Page 18, We contend that, due to effects illustrated by Marcolli et al. (organic liquid stable phase when multiple species are present) and the relatively large amount of water associated with inorganic components approaching saturation, very rarely will solubility limitation have any chance to affect activation.

Page 20, We know of no unambiguously demonstrated circumstance or theoretical physical reason why an expanded film should affect molecular transfer into solution. It is thought that, to effect equilibrium composition or kinetic uptake rate the impinging molecule needs to be screened from the bulk condensed phase in some way. An expanded film does not do this, by definition. There is a significant body of surface science literature demonstrating this. Of course, a "solid" or compressed liquid surface coating could affect equilibrium and kinetic effects.

Page 21, the unit has been corrected

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Page 21, the "\nu" is now consistent throughout

Page 22, Again, this is from an earlier version of the paper

Page 24, A reference to the Medina & Nenes study has been made

Page 24-25, The results are indeed interesting. This is not contrary to the possibilities in the discussion in 4.1.6, which contends only that expanded films cannot suppress equilibrium content. However, the Johnson study does indeed raise important questions. It may indeed be a coating effect or a bulk equilibration timescale effect, either of which requires investigation and explanation.

Page 25, Dr Leitch raises a good point here. On balance, it is probably only necessary to have CCN measurements under well-defined conditions which are in the range experienced during activation rather than trying to replicate what actually happens in a cloud. The section has been rephrased:

"This raises a further important issue. If HTDMA or CCN spectrometer measurements fail to allow sufficient time for particle equilibration, models based on prediction of equilibrium behaviour from composition will not be able to reconcile simultaneous composition and hygroscopicity or CCN activation spectrum measurements. Composition - hygroscopicity or composition - CCN closure will therefore be compromised. Ideally one would design an instrument to probe the response of a particle to saturation ratio in the same way that the particle will be exposed to a changing water vapour field below and in cloud. But such measurements, even when feasible, are very difficult to interpret given the range of possible aerosol particle histories in the atmosphere. Instead, one usually relies on models to predict particle growth and droplet activation. Accurate measurement of CCN (and CCN closure) under equilibrium conditions is not a sufficient condition for successful prediction of cloud droplet concentration. One still has to model the non-equilibrium conditions experienced by a population of particles growing and activating in a rising air parcel. Non-equilibrium size may derive from kinetic limitations associated with large particles, as well as from compounds that limit

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water vapour uptake. These effects must be captured accurately in cloud models, and possibly also in models that predict sub-saturated hygroscopic behaviour."

Page 25, We accept the comment concerning the surface tension effect, but this does not contradict or invalidate the statement.

Page 25, The Shantz et al. work has been referenced.

Page 26, We agree with the comment and the sentence has been removed.

Page 27, Low has been replaced by lower.

Page 27, The glutaric acid equilibration reference is added.

Page 30, The CCN closure references have been checked

Page 31, Wording corrected

Page 32, The point of the statement is that the prevailing wisdom is frequently driven by influential works. The low seasalt number concentration in the Charlson study, which leads to an overestimation of the importance of potential DMS-derived sulphate aerosols as CCN, influenced the Fitzgerald review paper on marine aerosols and much subsequent work. We have removed the reference to the Charlson paper, but attempt to maintain the context of the sentence: "This is a change from the previously widely-held view that sea salt particles are present at only about  $1 \text{ cm}^{-3}$ "

Figure 16 - we believe that the discussion is sufficiently detailed for objective review. If the referee thinks there is something wrong with the data or technique we will gladly answer the criticism. Firstly, we should clarify that only the winter 2004 data are unpublished, the summer 2002 data have been published in McFiggans et al., 2005 (we have replaced the top panel of the figure with that from this publication and this reference has been added to the figure caption). The winter data serve a valuable contrast to illustrate the seasonality. We do not see why we should remove sections from the paper simply because they are unpublished as they add valuable information to the

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discussion so we have left them in the paper.

Page 38, I guess this is a question of terminology. Kohler theory is an equilibrium calculation. On its own it cannot deal with disequilibrium effects. The phrase is reworded: "... cannot be quantified based on equilibrium Kohler theory alone"

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