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Interactive comment on "Inverse modelling of Köhler theory – Part 1: A response surface analysis of CCN spectra with respect to surface-active organic species" *by* S. Lowe et al.

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The authors present a new approach to assess the sensitivities of various parameters to CCN numbers. As opposed to numerous previous studies that used a 'one-at-a-time' approach, i.e. varying only one parameter at once, their use of response surfaces can reveal sensitivities over much wider parameter spaces. The focus on surface partitioning and surface tension and it is concluded that careful parameterization of these parameters is needed in order to successfully predict CCN under some conditions, in agreement with previous studies. The current study represents a model framework and the input data are artificially created so that perfect agreement can be achieved. So, therefore it is quite simplistic and does not lead to entirely new results. The sensitiv-

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Discussion paper

ity study for the selected parameters is more comprehensive and the approach might be promising to be applied to other problems in the future. However, not all parameters that have been identified as being important for determining the CCN numbers in previous studies have been discussed. Therefore, I think the paper's content and conclusions are somewhat weak and preliminary since only the suitability of the model framework, but not many new results are discussed.

The authors would like to take this opportunity to thank the reviewer for their constructive comments that we believe have added to the quality of the manuscript as a whole. The purpose of this study was to present a development of a new framework for probing sensitivity of aerosol activation to processes which have been studied in isolation over a number of years. The referee is absolutely right that there are a number of additional factors affecting CCN activation potential, but we focus on surfactant representations since not only is it a useful proof of concept demonstration of this framework, but there is still no clear message as to the wider relevance of surfactant behaviour. Using bulk to surface partitioning models, such as those presented here, previous studies have shown the impact of extreme behaviour, which one might consider as partitioning on or off, on the global scale, but suggested further studies would be better constrained by a wider parameter space such as provided here. In addition, as the referee points out, there are still studies promoting the potential for very low effective surface tension values, even if the concentration of surfactant material at activation might never be realised in the atmosphere. We feel demonstrating the use of a new multi-parameter sensitivity approach in helping to resolve the wider relevance of such issues is important, but requires incremental demonstrations of its use. We fully agree future studies need to tackle the issue of inter-instrument variability and process descriptions, but would also warrant much more data on systems for which we know the pure component and mixture properties more accurately than ambient systems. We hope our response to the detailed points below make this clear, as do recommendations for future work.

Our responses are presented in bold text following the reviewer's comments. Any referencing of sections, pages or line numbers given in the response pertain to those of the revised manuscript.

Major comments:

1. Mixing state In several previous studies, it has been emphasized that the mixing state of aerosol particles might be one of the most important parameters that determines CCN number in fresh air masses. While it has been addressed briefly in the manuscript, it should be discussed more thoroughly. Could a measure of mixing state be included in the model framework?

This a good point, CCN activity may indeed be influenced by the mixing state close to aerosol sources, and as such additional text and references have been added to section 3.1. The framework developed here could in principle be used for a treatment of externally mixed aerosols, however, the choice of mechanistic aerosol-cloud model would be important. In theory, frameworks such as PartMC-MOSAIC (Tian et al 2014) could be coupled with our MCMC approach. Furthermore, the methodology developed here could be coupled with a with multi-modal cloud parcel model in the future. One of the virtues of the framework built in the present study is that many different aerosol processes and characteristics can be included in the future for more specific case studies.

2. Previous study on CCN sensitivities In a previous study, Lee et al. (2013) have performed a sensitivity study on a global scale of many parameters using a MonteCarlo-based approach. This study should be discussed in the light of the results in the current study.

The Lee et al. (2013) is indeed an interesting study. However, due to numerous differences between our study and that performed by Lee et al. we feel that the study is not directly of relevance.

Firstly, the studies have different goals. The focus of this study is to construct a framework, based on inverse modelling methods, for which model input parameters non-measurable at the scale of interest (e.g surface tension) can be calibrated against measurements of CCN spectra, and ultimately that parametric uncertainty can be evaluated and constrained using MCMC analysis (part2). In contrast, the study performed by Lee et al. (2013) is concerned only with sensitivity evaluation. In this part 1 study, by testing the validity of the inverse approach through response surfaces, we also get a visualisation of the model's parametric sensitivity in terms of Objective Function (OF) response surfaces.

It is well understood that application of inverse modelling methodologies, both for model calibration and parametric uncertainty analysis, can result in (near-)identical model predictions for non-unique parameter values if the system studied contains parameters that are non-identifiable for the definition of calibration data used. In such cases it can be challenging for the applied algorithm to converge on optimal parameter values in an attempt to constrain uncertainties. Typically, such difficulties are approached by increasing the information content in the calibration data (synthetic or real-world measurements) (Vrugt et al 2001). Therefore, we choose CCN spectra as calibration data in the present study to maximise the available information content with respect to currently known observations - as compared with the single N50 value used in Lee et al. (2013). Appropriate definition of calibration data and the importance of information content is now discussed at some length in section 5.3 of the revised manuscript as an appropriate definition of calibration data is essential for successful application of automatic search algorithms for parameter calibration and parametric uncertainty analysis. In section 5.3 we have explored the implications of the information content contained within the calibration data for the identifiability of parameters investigated depending on the resolution of the calibration data, both with and without corruption of the synthetic measurements by a randomly generated natural variability. We conclude in the case of uncorrupted calibration

data that a typical 5-band CCNC spectrum would contain sufficient information content for the presented methodology, but that it is unlikely that the use of a single value would facilitate parameter optimisation. When also accounting for natural variability, only the high-resolution calibration data, as used in the present study, would suffice for correct minimisation of the OF.

The dissimilarity in the definition of the calibration data between the present study and Lee et al (2013) is a natural consequence of another difference between the two studies – the scale. Our study is focused on developing a process model framework suitable for further uncertainty analysis in closure studies using algorithmic approaches, and we have referenced to similar studies accordingly Partridge et al. (2011, 2012). Such a study provides us with the opportunity to scrutinise the necessity for complexity, at a level of Köhler theory, offline whilst maintaining computational efficiency. Consideration of the impact of bulk atmospheric parameters (e.g. emission rates), as seen in Lee et al. (2013), does not fall under the remit of the present study and instead we choose to highlight the importance of Köhler model complexity in GCMs for the most accurate predictions of CCN. To summarise, any sensitivity methodology relies heavily on the choice of calibration data. The focus of the present study is the construction of a framework for an inverse modelling approach to parametric uncertainty analysis and model calibration for entire CCN spectra at a process level rather than a single value on a global scale. Therefore, it is of our opinion that in some sense the present study is both more complex and robust in relation to potential model-observation evaluation and depth of process treatment. By performing this kind of analysis over a range of supersaturations the global climate modelling community can gain a lot from the end results.

Therefore, owing to the dissimilarities in methodology and purpose of the two studies, and that Monte-Carlo methods have not been employed here in part 1, direct comparison of results with respect to sensitivity is not possible and thus

we have chosen to cite appropriately and not discuss Lee et al. (2013) at great length within the manuscript.

3. Uncertainty in cloud formation The authors state correctly that for data sets other than their calibration data set as used here, a perfect agreement cannot be expected. Some discussion on how accurately CCN numbers should be predicted should be added. For example, all measurements are associated with some measurement error. In addition, other factors influence CCN number (e.g. Lee et al. (2013). Given all uncertainties in the current abilities to predict cloud formation (meteorology, updrafts, emissions, etc), what is the recommendation for a tolerable uncertainty in CCN predictions?

The reviewer makes an excellent point regarding the treatment of errors and acceptable uncertainty. Following a similar request from reviewer 2, additional material has been added to the manuscript in section 5.3. Therein we have discussed at length the importance of information content for various definitions of the calibration that may arise due to different instrumentation. We also account for the natural variability in these considerations. It was concluded that, when accounting for natural variability in the analysis, the typical supersaturation resolution of CCN counters used in-situ would be challenging to correctly minimise the objective function as done when using the high-resolution spectra as seen in the present study. As natural variability in CCN measurements is typically on the order of tens of percent this effect will dominate over any instrumentation errors introduced, counting errors as deduced from Poisson statistics, for example. Thus we choose to focus on natural variability in this study to illustrate this point.

4. Solubility In previous studies, the solubility of organics has been identified as an influential parameter (Riipinen et al., 2015). However, this is not even mentioned in the current paper since all organics are assumed to be completely dissolved. How would consideration of a range of solubilities change the conclusions?

We agree that solubility may play a role, as will mixing state, gas to particle partitioning, condensed phase reactions and mass transfer limitations according to an amorphous condensed phase, depending on the RH history of the particle distribution in question. In this framework, the solubility would change the single particle hygroscopicity that would need to be constrained by an equivalent parameter space to the one presented here. This would need to be coupled to an appropriate gas phase mechanism since the solubility spectrum, such as that presented by Riipinen et al (2015), is driven by the specific abundance of compounds within different volatility ranges. We would argue then that any treatment of solubility should also be coupled to a model that can treat gas to particle partitioning since the most thermodynamically stable state of a framework that does not allow partitioning might never be met, affecting the derived parameter sensitivity. Such a model framework is beyond the scope of this study, but for sure warrants future investigation. Again, in theory this framework could be wrapped around any mechanistic or semi-empirical model, the results of this stepwise study demonstrating its use.

5. Surface-active fraction The discussion of previous studies on the effect of surface tension to CCN activation is somewhat confusing. For example, studies by Noziere et al are discussed that reveal surface tension of 30 nM on aerosols. This number, however, is not relevant for CCN activation unless sufficient material is available to cover the complete particle/'droplet near activation. I suggest discussing the cited references more carefully. What fraction of surface-active material is needed to cause the effects as seen in the current study? Are these fractions realistic?

The reviewer has raised a very good point here. This issue is relevant for Köhler frameworks 1 (traditional Köhler theory) and 2 (redistribution of surfactant concentration and a concentration-independent fixed surface tension). One of the key results of this paper is that the complete partitioning framework (4) produces CCN spectra and response surfaces similar to traditional Köhler theory

as a consequence that surface tension is often very close to that of water at the point of activation and largely insensitive to the partitioning parameters used in the Szyszkowski equation. While this result is perhaps well known in the communities of the references in question, it is arguably less well known in the cloud physics community. Text relating to the references has been reformulated and revised, and the result has been discussed more carefully.

6. Figures Several figures appear blurry and hard to read due to very small font, e.g., Fig. 1 and 3: the indices in the legend are hard to distinguish Fig. 4: Avoid putting the legend box across the lines in the figure

We apologise for this – these figures have now been remedied.

Technical corrections:

All minor comments have been addressed, as advised, in the revised manuscript. Thank you for taking the time to bring these to our attention.

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