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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Global distribution of the effective aerosol hygroscopicity parameter for CCN activation" *by* K. J. Pringle et al.

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Response to reviewer 2

We thank the reviewer for the constructive review of the manuscript.

In response to the comments:

The model fields are not shown; they are to be presented in another paper where comparisons to observations will be made. This is somewhat of a concern because the calculations in this paper are only meaningful to the extent they reflect observed aerosol composition. However, since the models used are well known and tested, presumably the fields are reasonable.

We agree this is a limitation of the paper. To show that the fields are reasonable, we do give a short summary of the comparison to other models and to observations (page 6305). We can also confirm that the ECHAM/MESSy Atmospheric Chemistry model has been used in a large number of published studies.

Assuming this, mostly the results shown here are not surprising, since they reflect current knowledge of the composition of the fine fraction of the atmospheric aerosol, which contains most of the number concentration and thus influences CCN concentrations most strongly.

It is of course true that Kappa is a direct result of the particle composition, and although there may be few "surprises" in the fields it is the first time global fields of Kappa have been made available, we feel these fields will be useful to those in the community who are interested in particle activation, but do not have access to aerosol composition fields from a global aerosol model. Our global results may thus provide guidance to field measurements by providing the large scale perspective. We also feel it is important to stress the limited representativity of surface measurements for CCN at cloud base, which has not been mentioned in earlier work, as also noted by the reviewer.

The authors do make a good point regarding the variations in composition with height and noting that in general, hygroscopicity decreases with height, either because an enhanced fraction of organic species or of dust is present. Since these altitudes are most relevant to cloud formation, surface CCN measurements may not provide a complete or accurate picture of how aerosols affect cloud formation.

Overall, if I have understood this presentation correctly (see below), the findings presented here really present global variations in bulk, fine mode aerosol composition, as reflected in the hygroscopicity parameter (whose calculation is somewhat uncertain, especially for the assumed single value for the organic fraction). These fields cannot be immediately translated into CCN concentrations, even

given fine aerosol size distributions, unless the assumption of complete internal mixing is valid. The authors' earlier papers have explored the validity of these assumptions for some observational data sets, and the validity of this assumption on the global scale needs to be shown here – or at the very least, the authors should make more clear that CCN predictions using these recommended values are valid for only very aged, internally-mixed particles.

We address the point of CCN calculation / internal mixing in more detail later in this response, however, we would like to note that we agree that the question of internal mixing is an interesting one, but it is also an extensive study in itself and we feel that a full discussion of it is out with the scope of this paper. We are, however, currently preparing a follow-up study which examines the sensitivity of simulated CCN fields to Kappa and assumptions about the aerosol mixing state.

Most of the questions I have for the authors refer to Section 2.2, where the calculation of kappa is discussed. First, the mixing rule as presented is valid for an internally mixed aerosol, and it is stated that this rule has been applied to each of the seven aerosol models of the model. So is it assumed in the model, or perhaps only in these calculations, that each simulated mode is completely internally mixed? This is an important point that must be stated explicitly – it is not explained in section 2.1, Model Description.

A Kappa value for each mode is calculated using Equation 1. We then average this modal Kappa over the CCN active and inactive particles in the Aitken and accumulation modes to give one overall Kappa value.

Page 6305, Line 10, we have added the line "The 4 hydrophilic modes comprise a nucleation, Aitken, accumulation and coarse modes, the 3 hydrophobic modes are Aitken, accumulation and coarse modes. The aerosol composition within each mode is internally mixed, but the 7 modes are externally mixed with respect to each other, and notably the hydrophobic and hydrophilic modes are chemically distinct."

Also, please note that although the kappa values assumed for each component are listed, one needs also the assumed densities in order to compute volume fractions from the modeled mass fractions.

The densities have been added to Section 2.2.

Second, it is stated that "We calculated kappa for each of the seven aerosol modes of the model. [in Section 2.1, these are identified as 4 hydrophilic and 3 hydrophobic lognormal modes, but it's not clear how these are related to the "Aitken," "accumulation", etc. modes?]. We took the volume weighted mean value of the Aitken and accumulation modes as this size range is most relevant for atmospheric CCN concentrations in the atmosphere and thus for comparison to field observations. . . . We considered the volume fraction of each component in both the hydrophilic and hydrophobic modes, which corresponds to the bulk composition of fine particulate matter".

So if I understand the above correctly, what was done was equivalent to a filter-based estimate of aerosol hygroscopicity: The contributions of the nucleation and coarse mode were ignored, and the rest of the aerosol mass (which essentially would show up on a PM1 filter) was assumed completely internally mixed, and then kappa was calculated? If the approach was this simple, then the discussion needs to be revised to make this clear. It's confusing to talk about how each mode was treated, if this information is not really used. Further, if indeed this simple approach was used, why go to all the trouble of using a size-resolved aerosol module to simulate the aerosol composition? Since the authors do have more resolved information, however, it seems like an opportunity was missed here to discuss what the model predicts as far as mixing state and chemical heterogeneity and where that matters for the estimation of CCN concentrations.

We use a 7 mode model as the modes have distinct atmospheric lifetimes, as determined by their different removal rates, which justifies their individual treatment in the

model.

We have altered Section 2.2 in order to clarify the description of the Kappa calculation and we have added Equation 2 which explicitly shows how we take the mode dependent Kappa values and average them to give an overall Kappa value.

We agree that consideration of the mixing state is also interesting and we are addressing this in a follow up study, but the purpose of this paper is to give a broad overview of the distribution of Kappa. Averaging Kappa over the CCN active and inactive modes is the most efficient way to give a clear overview of the effective overall hygroscopicity of aerosols in one value or one map. It is also the approach used by Andreae et al (2008) when they suggested the average global mean marine and continental Kappa values that we discuss in the text (page 6307, Line 23) and the value reported by most observational campaigns.

By presenting in the supplement maps and tables calculated Kappa calculated using CCN active aerosol only, we do give some discussion on the mixing of the aerosol. We show the difference in Kappa that occurs when CCN inactive aerosol are neglected, which has previously been shown for individual locations, but not globally.

Although on p. 6306 the authors cite a number of papers that they say support a bulk composition approach as adequate for the prediction of CCN concentrations, I don't think this has been uniformly found in prior closure studies (e.g., Cubison et al., 2008, suggested that knowledge of the mixing state was of primary importance in determining the activation properties of urban aerosols). I have difficulty understanding how the information presented here can be extrapolated to the accurate global prediction of CCN concentrations, using simulated size distributions, as implied in the manuscript.

We agree that the step from the presented fields to the calculation of CCN is a tricky one. A number of studies have shown that in observational studies that reasonable CCN closure is possible when a single Kappa value averaged over all CCN active and

inactive values are used (see references listed in 6306, line 24). But, Cubison et al. (2008) found that in Los Angeles the mixing state must be taken into account in CCN calculations and thus concluded that mixing state may be important in urban areas. Other studies in urban regions (e.g. Rose et al 2010), however, have achieved good CCN closure without considering the mixing state.

We feel the subject is one of ongoing study and that although the approximation may not be universal it has been shown to be appropriate in many regions.

To clarify the degree of uncertainty we have added the Cubison et al., 2008 reference and the following caveat:

"However, by calculating a mean Kappa averaged between the hydrophobic and hydrophilic modes we loose information on the mixing state of the aerosol, which may lead to biases if these fields were to be used directly to calculate global fields of CCN in regions where there is a high degree of external mixing (e.g. urban regions, see Cubison et al., 2008)."

In addition we state that the approach is appropriate for "**approximate** calculations of CCN".

Specific comments:

Abstract:

1. When the mean values are presented, it should be noted that these were based on assumed internal mixtures of the fine mode aerosol (if that was indeed the case).

Added:

"These values are the internally mixed Kappa calculated across the Aitken and accumulation modes."

2. "The influence of industrialisation on aerosol hygroscopicity appears to be

less pronounced than the influence on the aerosol burden". On what basis is this statement made? The mass loadings? But that is not totally relevant to number concentrations. The sensitivity of the predicted CCN at some selected supersaturation would be a more relevant comparison. The sensitivity of Kappa against supersaturation may be more appropriately addressed with a cloud resolving model.

We have removed the line "The influence of industrialisation on aerosol hygroscopicity appears to be less pronounced than the influence on the aerosol burden" from the abstract as we agree that it is confusing.

3. Last sentence (and elsewhere): the factor change of kappa is not the most relevant metric, since for example a factor of 2 could mean 0.6 to 1.2 or 0.001 to 0.002, having very different magnitudes of impact.

We have added reference to the initial value in the abstract:

"factor of 2-3 above the initial value of approx. 0.005" (page 6303 line 2).

2.1 Model description

1. T42 resolution is approximately 2.8 by 2.8 degrees, considered coarse resolution. This should be pointed out, because many fields will be "smeared" due to this factor alone.

Pg 6309 we have re-worded line 10

"The low resolution of the global model (T42) will underestimate the horizontal variability of Kappa, with values averaged over large grid-boxes (approx. 250 km), but even if this effect is considered, the rate of change of Kappa across a geographic region is quite low, with regions of thousands of square kilometres showing quite constant annual mean values."

3.1 Comparison with observations

Much of this discussion would be the same for an earlier-generation model that predicted only aerosol mass concentrations in the fine mode. The contrast between continents and oceans is expected, as are the plumes of pollution that modify aerosol composition in certain oceanic regions.

We agree with the reviewer on this point, but we note that although the ocean-continent contrast is not unexpected we feel that the horizontal and vertical distribution is perhaps not as well known throughout the wider community (including the observational community).

3.4 Annual cycle

1. "the chemical composition can change throughout the year, which can potentially affect kappa": isn't it certain that it will affect kappa?

It is certainly likely, the exception being that varying the composition of the inorganic species will have little effect on Kappa as ammonium sulfate and ammonium nitrate have similar kappa values.

2. I can't accept that the seasonal cycle is not important. One has to only look at the data collected by the IMPROVE network at rural sites in the US to see that there is a strong seasonal cycle in composition that must certainly affect kappa.

Page 6312, Line 1-2. We have deleted the statement: "implying that seasonal variability may be less important over a large scale than the site specific variability"

3.5.1 Regional distributions, continental

1. p. 6312, line 18: I don't agree with this reasoning. I would guess that the coarse resolution of the model is responsible for much of the homogenization that is observed, and it is not accurate to ascribe it to an actual physical process without much more checking against observations. A similar comment applies to p. 6314, line 10.

We have removed the statement:

Page 6312, line 17-18 “This implies that inland on a large-scale annual average it may be well characterized by a single value.”

page 6314, line 9-10 has been re-worded:

“In most regions the standard deviation of Kappa due to time variability is small compared to the deviation due to variability within the region implying that, if a choice has to be made, it is better to focus analysis and measurements on the regional (rather than temporal) distribution of Kappa. N. America, however, has a more pronounced seasonal cycle than the other regions – Kappa values range from 0.4 to 0.2 with a minimum in June and July. A similar cycle is found in the N. Atlantic. In these regions the standard deviation due to variations in time (t5) is larger than that due to area (x, y), for example in N. America St Devx,y = 0.05, St Devt5 = 0.07. In Europe, the standard deviations in space and time are of a similar magnitude (St Devx,y = 0.08, St Devt5 = 0.05), thus temporal variability in this region can also not be neglected. This analysis implies that longer term measurement campaigns are particularly required to characterise Kappa in N. America, N. Atlantic and Europe, although every region shows some variation due to the annual cycle, thus long term measurements would be advantageous. In general, regions that experience a strong annual cycle (i.e. the midlatitudes) will clearly experience the strongest temporal variability in aerosol composition (and Kappa)and thus long term measurements would be advantageous. ”

3.5.3 Regional vs. temporal variability

1. p. 6314, line 12: the minimum in kappa in North America in June and July is quite surprising, and I would guess inaccurate for the Eastern U.S. Again, a lot of information is based on modeled chemical fields that are not shown and, until the companion paper is published, cannot be evaluated against observations.

We agree that this is a limitation of the paper, we intend to do additional comparision

with observations (including longer term observations of Kappa) in the future.

3.6 Effect of regional mean kappa on critical supersaturation required for CCN activation

1. The study by Reutter et al assumed a single, chemically uniform lognormal mode. Thus, the findings cited here are fully relevant only to the extent that the atmospheric aerosol conforms to this picture.

Page 6315, line 10. We clarified that a single lognormal mode was used by Reutter: “for a typical biomass burning aerosol size distribution (assuming a single lognormal mode) using a cloud parcel model”

2. Figure 7 reinforces the idea that the aerosol can be considered chemically homogeneous, and that this single value together with the modal size distributions can be used to predict CCN active at any supersaturation. Is this indeed what the authors are claiming?

Figure 7 was designed to place the differences in Kappa in the context of activation, so that the differences could be understood in real terms. For that reason we use the example of a single particle of a particular size (not a population of particles).

The figure is similar to a figure shown in Andreae et al (2008, their Figure 5) who summarised observed Kappa values and used these to show the range of critical supersaturations required to activate aerosol measured in marine, continental / urban and moderately aged pyrogenic aerosol.

We add to this analysis by showing the relationship derived from model data for different geographical regions, which we feel is a useful extension to the original plot by Andreae et al (2008).

I also want to ask about the statement on p. 6316, line 13-15, that although particle size is the main factor in activation, the small differences in kappa between regions can also play a role. I find it hard to believe that these variations in the

mean kappa matter more than external mixing with modal differences in kappa. Can this hierarchy of importance be demonstrated for the ranges of situations modeled here (ie the actual mixing states / sizes of various modes and compositions)? That would be a fascinating and highly useful result.

As far as we are aware no one has examined the effect of internal / external mixing on Kappa and CCN in a global model, so it is difficult to comment on which is more important, but we agree it is a very interesting (but quite extensive) subject that we plan to address in a follow-up publication.

3.7 Present vs. Pre-industrial

p. 6318, line 7-9: Doesn't one have to weight changes in number, diameter AND composition to really understand these differences? It seems like this analysis is oversimplified.Similar comments apply to the note about applicability of mass-dependent parameterizations.

We agree that to calculate the change in CCN one must consider number, composition and size. This analysis has been done in a number of published model studies. Here we try to isolate just the change in hygroscopicity to give an idea of how this has changed since pre-industrial times. This effect is more subtle, but has implications for sub and supersaturated water uptake. It is our opinion that the change in water uptake ability between preindustrial and present day aerosol is not something that is widely known.

We have removed the comment on empirical relations (Page 6318, Line 15 – 17).

We have also added the line: pg 3618 line 17:

"However, the implications for this on CCN cannot be assessed without also considering the change in the aerosol number and size distribution that has occurred."

References M.O. Andreae, D. Rosenfeld, Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, Earth-Science Reviews, Volume

89, Issues 1-2, July 2008, Pages 13-41

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