**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "A single parameter representation of hygroscopic growth and cloud condensation nucleus activity" *by* M. D. Petters and S. M. Kreidenweis

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General Response to All Reviews

We thank the 5 reviewers of this manuscript for their insightful and helpful comments. In particular, all of the reviewers commented on the need for a better description of how our approach relates to prior work in the literature. We agree that the paper is much improved by such an addition, and the newly-added Section 2.2 represents our efforts to trace the historical context, improve our citation of the relevant literature, and explain under which conditions prior methods are essentially equivalent to the fitting of the kappa parameter.

We particularly appreciate the comments of Drs. Svenningsson and Swietlicki, who

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Discussion Paper

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alerted us to the prior work of Rissler et al. (2006) which used a parameter with a similar conceptual basis, also called kappa. Our somewhat unfortunate choice of the same symbol was coincidental. The similarities between these approaches are now described in Section 2.2 with appropriate references.

With respect to the overall intent of this paper, we agree with the comments of Referee #1, who noted that the strengths of this contribution are (1) explicitly linking the sub- and supersaturated regimes, via relatively simple equations that do not break down for cases of low or zero hygroscopicity, (2) the tabulation of fit parameters for many relevant species based on both HTDMA and CCN measurements, which is useful for modeling and also serves as a check for consistency between the sub- and supersaturated regimes, and (3) the testing of the mixing rule using published data.

In the following we provide individual replies to each review.

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Anonymous Referee #1

- Relating the proposed approach to other single-parameter hygroscopicity representations is very important.

As noted above, we have added a section that addresses this.

- The κ-Köhler theory proposed here can be used with field determinations of aerosol composition to derive values of kappa which are appropriate to various types/groups of bulk organic species. Several techniques are starting to routinely determine the groups of bulk organic species present in ambient aerosols, such as functional groups from FTIR [Maria et al., 2003], HOA and OOA from the AMS [Zhang et al., 2005], or various categories from WSOC-NMR [Fuzzi et al., 2001]. The approach presented here allows the linear mixing of the kappas from each organic group. If the values of kappa derived through this method are shown to work for varying mixtures the same organic groups as measured in different environments, the combinations of these techniques will provide a very important shortcut for the representation of organic hygroscopicity and activation in models. This exercise would also allow the detection of deviations where such a parameterization is insufficient. I suggest that this possibility is referred to in the paper.

Kappa certainly provides a framework that can be used to test whether various measurements (functional groups, principle component mass spectra, or NMR spectra) have predictive power for organic aerosol hygroscopicity. Similarly, emissions based estimates of hygroscopicity (e.g. biomass burning, biogenic SOA, etc.) and their mixtures, may also be tested. As suggested, we now include these possibilities in the revised version (see Section 5).

- The abstract (line 13) states "We confirm the general applicability..." of this approach. It seems that this is slightly overstated, and that the remaining uncertainties are better captured in the conclusions section. Since the paper is short and since many people will only read the abstract, I recommend explaining the current limitations and future tests in more detail in this section.

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We lengthened the abstract to include more detail, and also deleted the word "general" because this requires further testing of these methods in the laboratory and field.

- P 8441: at a recent conference I saw a report of non-linear mixing effects appear when mixing a surface active (HULIS) and a non-surface active (ammonium sulfate) component. It seems that this type of effect would not be captured by the κ-Köhler theory.

Several reviewers asked about the treatment of surface tension. We have rewritten the description of how we treat surface-active compounds, and hopefully this is now more clear. In brief, the value of kappa returned by a fit to data depends on the choice of non-fit parameters in Eq. 7, namely, temperature and surface tension. We consistently assume $\sigma_{s/a} = 0.072$ J m^{-2}, which leads to estimated hygroscopicities that are consistent with this assumption. For surface active species, the effect of the assumption is to cause the fit kappa value to be larger. However, any self-consistent set of kappa/surface tension should reproduce the original data. In mixtures, some surfactant activity for this component is thus accounted for. It is possible that the non-linearity of mixing that the reviewer refers to does not have a large enough effect on the mixture kappa to exceed uncertainties in the data as expressed in Fig. 3. Certainly, further studies of whether kappa is sufficient to account for surface tension effects are warranted.

- P 8439 / line 6: what is referred to here as "sphere equivalent diameter" is typically referred to as "volume equivalent diameter" (Dve) in the aerosol literature, see e.g. DeCarlo et al. [2004].

We changed the wording as suggested.

- P 8443, line 2: the observation that size is more important than chemistry for CCN activation was first given by Junge and McLaren (1971) and further explored by Fitzgerald (1973). The former paper should also be acknowledged here. (By the way this was a long time before the recent re-discovery of this result by Dusek et al!)

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Discussion Paper

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We have added all of these references (plus some additional ones) to Section 2.2 and Section 4.

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Anonymous Referee #2

- The paper is in general confusingly written. The key issue in this paper is not a new form of Köhler theory (kappa-Köhler theory), but a new way of expressing water activity. Kappa seems to be a non-Raoult formulation of a volume concentration activity coefficient. This in itself is a very interesting approach, simplifying calculations done on particles consisting of complex mixtures. This focus on activity coefficients should be clearer in the paper in general as well as in the abstract.

- It would be informative to show how kappa relates to traditional Köhler theory; how is this method of describing water activity related to other ways to describe it?

The reviewer is correct that the central idea is the parameterization of water activity with the single parameter kappa. As we now explain in Section 2.2, the water activity expression is still traceable to Raoult's law. However, it is also true that using volume as the independent parameter is more useful, since it is the "native" variable of HTDMA and CCN measurements (i.e., measurements are done for a particular dry diameter which can be converted into volume, and in the case of HTDMA data, the volume of water at each RH setpoint is measured). This eliminates the need for assumptions about density and molecular weight when fitting the data - i.e. measured variables can be input directly without conversion to mass or moles.

We hope the new Section 2.2 serves to address at least in part the Reviewer's concerns in both of these comments.

- Why is the upper value of kappa equal to 2?

- Why is it claimed that kappa is between 0.01 and 2 when tables 1+2 do not show any values above 1.4 (even for NaCl which has the highest value of 1.33 derived from growth factor measurements)

This is a good question. We initially chose the value 2 because it is not clear whether there are atmospherically relevant compounds that are more hygroscopic than sodium

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chloride ($\kappa \sim 1.33$) and if so how large the uncertainty bar might be. To explore this further, we added additional inorganic species to the Table. Based on the expanded results in Table 1, we believe we are justified in changing the stated estimated upper limit to $\kappa \sim 1.4$.

We have now also added to the text estimates of κ from a few field studies to give an idea of the range of typically-observed values for actual atmospheric particles.

- In Equation 1 the density is written as the density of water, is this not an assumption? Should this not be the density of the solution?

In the classical derivation of Köhler theory the partial molar volume of water in solution appears in the numerator. Under the assumption of volume additivity the partial molar volume equals the molar volume of pure water, and thus the density of pure water appears in the Kelvin term. Please see Kreidenweis et al. (2005) and references therein for further discussion.

- Equation 6 seems to have a "switch" behavior when kappa is around 1, is this true?

No. The equation has no discontinuities for any values of kappa over the range from 0 to 1.4. As κ increases larger wet particle diameters are required to establish equilibrium at any given saturation ratio. This is consistent with more hygroscopic species having larger water contents.

- The point 1:2:2 levoglucosan:succinic:fulvic in figure 3 does not correspond to the value given for kappa in table 3 (0.123,0.163). Which one is correct?

Unfortunately the labels of 1:3:3:3 levoglucosan:(NH4)2SO4:succinic:fulvic and 1:2:2 levoglucosan:succinic:fulvic in Figure 3 are swapped. We corrected this mistake in the revised version. Thank you for pointing this out.

- In the summary and conclusions section it is stated that "This approach appears adequate for predicting CCN activity of mixed particles having appreciable amounts of strongly surface active materials, but the generality of this assumption requires further

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verification." What is meant by adequate? For which purpose and by what means is this determined?

Our intention is that "adequate" expresses that mixing rule predicted and directly observed hygroscopicity agree within measurement uncertainties. We reworded the sentence accordingly.

- The first sentence in the final paragraph "Although the focus of this paper is on characterizing the CCN activity of atmospheric particulate matter, it is possible to also derive values of kappa from other types of data, such as hygroscopic growth factor data obtained from an HTDMA" is off balance. The sentence should be rewritten as it is not apparent that this is the focus of the paper.

We reworded the sentence.

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R. Leaitch (Referee #3)

- Page 2 - "but it was recognized some time ago that less- and non-hygroscopic organic compounds can contribute substantially to, and sometimes even dominate, atmospheric aerosol mass concentrations." Reference needed.

We added a reference to Kanakidou et al.(2005) who presented a comprehensive review of atmospheric organic aerosols.

- Page 5 - equation labelled (9) should be (8).

Thank you. We have also added additional equations and have checked for proper numbering and citation.

- Page 5 and Table 2 - It appears that you use one sigma for your uncertainty estimate. Assuming the sample size is large enough, this encompasses only about 67% of the variation - two sigma would be better.

We state that we use a one standard deviation uncertainty estimate. A two-standard-deviation error bar can be easily constructed from this information, and would of course appear very large in Figs. 3 and 5 - which is a point well taken!

- Page 6 - "to apply bulk sample-based parameterizations to curved droplets." Presumably, the authors are referring to measurements of surface tension of bulk solutions. This should be stated a little more precisely.

We reworded the sentence, and changed the discussion of surface tension effects to hopefully clarify it.

- Page 6-7 - section 4 - It is first stated that "In general, however, the experimental data for water activities over the full range of solution concentrations cannot be well-fit with Eq. (2) using a constant κ. Two sentences later it is stated that "Extrapolated $s_c's$ using this or similar methods (e.g. Svenningsson et al., 2006) are in good agreement with measured $s_c's$ for many, but not all, particle types studied thus far". I have trouble

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reconciling these two statements, i.e. they seem to me to be a bit contradictory. Please explain, and revise as necessary.

The statement "Extrapolated $s_c's$ using this or similar methods (e.g. Svenningsson et al., 2006) are in good agreement with measured $s_c's$ for many, but not all, particle types studied thus far" refers to methods that use multiple fit parameters (e.g, a polynomial) to represent the same properties that we fit with kappa (or an equivalent parameter).

We know that the hygroscopicity parameter varies with aerosol water content. This variability is the result of solutions behaving less ideally for more concentrated solutions. Thus a constant value of κ derived from CCN activity, where the solution is dilute, does not in many cases match the hygroscopicity at 60% or 90% RH, and consequently the growth factor relationship cannot be well-fit using Eq. (2).

However, the goal from an aerosol-climate interaction perspective, is to predict the number of activated droplets in an updraft. Our hypothesis is that small, and in some cases, moderate variations in κ have little to no effect on the fraction of activated droplets, when the activation of a population of particles in a parcel experiencing changing supersaturations is simulated (Ervens et al. 2005; Koehler et al. 2006). Thus, we speculate that a constant κ is likely "sufficient" (i.e., within experimental uncertainties, or close enough to result in minimal changes in computed quantities such as activated fraction) to adequately treat aerosol-water interactions in both the sub- and supersaturated domains.

In the manuscript, we test this speculation by comparing kappa values derived from CCN and HTDMA measurements, including measurement uncertainties. For the data presented in the manuscript the level of agreement is generally within experimental errors and probably within the range of $\delta\kappa$ for which minimal effects on activated drop fractions are observed. However, the resolution in κ that is required to address outstanding problems in aerosol indirect effects on climate is not yet well-established, and further research on quantifying acceptable uncertainties in κ is needed.

Interactive
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Discussion Paper

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- Page 7-8 - First, it is stated that there are no measurements of the HGF for adipic or succinic acid, and that a κ of < 0.006 is based on the detection limit of the HGF method. Two sentences later, it is stated that "the hygroscopicity of succinic and adipic acid is fairly large ($\kappa > 0.1$)", I think I understand how the first estimate is made, but I see no reference or data for the second of these statements. Again, please explain.

We reworded the section and now explicitly refer to the data summarized in Table 1:

"For some of the compounds shown in Table 1, e.g. adipic or succinic acid, no water uptake is observed in the subsaturated domain. The current detection limit for the diameter growth factor measurement is ~ 1.02, translating to a lower limit of $\kappa \sim 0.006$ that can be observed in an HTDMA, with a similar limit for the electrodynamic balance. A quick comparison between growth factor derived and CCN derived κ values for these compounds shows, however, that $\kappa < 0.006$ does not match the much larger values inferred from their CCN activity. While the CCN derived hygroscopicity of succinic and adipic acid is fairly large ($\kappa > 0.1$, cf. Table 1), their solubility in water, i.e. the mass of solute that can be dissolved in a given amount of water, is small. Accordingly, the water activity of the saturated solution is large, thereby raising the deliquescence relative humidity, for small particles sometimes exceeding values of 100%. The equilibrium water content of a succinic acid particle at $a_w > 0.9$ corresponds to a metastable state where the concentration of solute exceeds the solubility limit. Thus, for an initially dry succinic acid particle no water uptake can be observed."

Full Screen / Esc

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Anonymous Referee #4

- Introduction: Make the paragraph flow better.

We reworded the introduction accordingly.

- As said in the paper, it has been found that organics contribute substantially to the mass concentrations of aerosols. Reference some papers.

We added a reference to Kanakidou et al. (2005) who presented a comprehensive review of atmospheric organic aerosols.

- In paragraph 2, what insufficient data? Be specific like molecular weight, dry particle density, etc.

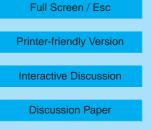*We have added this as suggested.*

- Define Dd as dry diameter.

We added the definition.

- In Figure 1, κ values are shown down to 0.001. It is said that for $\kappa > 0.01$ have a slope of -3/2. What slope does the constant κ line have for values of $\kappa < 0.01$. What is responsible of changing the slope?

We have now modified the discussion of the slopes to hopefully make this more clear:

"The curves follow the expected Köhler slope of $\sim -3/2$ (Seinfeld and Pandis, 1997) when $\log(D_d)$ is plotted on the abscissa and $\log(s_c)$ on the ordinate, for $\kappa > 0.2$. As κ approaches zero, the particle becomes nonhygroscopic and the slope approaches that expected for an insoluble but wettable particle as predicted by the Kelvin equation, i.e. -1. This can also be seen mathematically from Eq. (6): for $\kappa = 0$, the water activity $a_w = 1$, representing wetting of the dry particle by a pure water film, and Eq. (6) reduces to the so-called Kelvin equation. In the intermediate range $0 < \kappa < 0.2$ lines of constant κ are slightly curved, and have the asymptotic slope of -3/2 only for large

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Full Screen / Esc

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Interactive Discussion

Discussion Paper

particles. *This curvature arises from the non-negligible contribution of the initial dry aerosol volume to the total volume of the droplet when the equilibrium water content is relatively small."*

- Derivation of κ values for atmospherically-relevant species and particle types: How do you know what is the range for inorganics, hygroscopic organics and nonhygroscopic organics? Is this range based from calculations, observed data, literature values? If it based from literature reference it.

A complete list of the individual components and other particle types (e.g., SOA) that were studied, including references, appears in Table 1 and was used, together with estimated kappas from a few field studies, to estimate the ranges quoted.

- Again you mention up to κ values of 0.01, what species would fall in $0.001 < \kappa < 0.01$ range?

Chemically aged diethylhexyl sebacate, and insoluble particles that are coated with trace compounds of nitric acid fall into this range (Petters et al., 2006). We have added them to Table 1.

- Table 1 should be written in the form of instead of κ_{low} and κ_{up}.

There is something missing to this comment.

- Give reasons why you are assuming the surface tension of water. Also were there any surface tension measurements done in the papers you cite in which you can compare if κ is affected?

We have revised our explanation for the choice of surface tension used in the fitting, and it is hopefully now more clear (please see Section 3).

- Figures 1 and 2 could be put together.

We prefer to keep the figures separate; Figure 2 would not be legible with the addition of all constant-kappa lines within each decade.

- In Figure 3, mention Equation (7) as the linear mixing rule used.

We now mention Equation (7) in the caption of Figure 3.

- In Figure 4, write particle consists of ammonium sulfate and non-hygroscopic organic.

We changed the caption accordingly.

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B. Svenningsson and E. Swietlicki (short comment)

Thank you for your comments that helped us improve the paper.

As you note, it is indeed important to stress that the "insoluble fraction" that appears in some studies is dependent on the choice of model salt used in fitting, and self-consistent choices must be applied when using the fits in other calculations. We have added this key point to the text.

We have already commented above on most of the points you have raised, except we have one additional comment re the following:

"We do not have a strong opinion about which of these parameters (epsilon, kappa (Rissler et al. 2006), kappa (Petters and Kreidenweis 2006),or Bc) to use, since they all are similar and depend linearly on each other."

We certainly agree that the parameters can be readily related to each other, when they have been derived from a water activity basis using a "full" version of the Köhler equation, and that all are equally useful. The one exception to be noted, which we point out now in the text, is when CCN measurements have been fit to the maximum of the approximate equation

$$s = 1 + \frac{A}{D} - B\frac{D_d^3}{D^3} \tag{1}$$

where s is the equilibrium supersaturation expressed as a fraction and A is essentially a constant at constant temperature. For most atmospheric observations, the B parameter fitted to data using this equation will be equivalent to kappa. However, in the case of low hygroscopicity, this equation may lack sufficient accuracy (as we now discuss in the text) and our equation (6) or an equivalent expression should be used for fitting.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 8435, 2006.

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