

## General comments

Yun et al have included a new treatment of black carbon in the CAM-IMPACT GCM, which distinguishes hydrophobic, hydrophilic and hygroscopic particles by the existence and thickness of the sulfuric acid coating on these particles. Different ice nucleation abilities in the mixed-phase temperature range are assigned to these particles, and the resultant aerosol indirect forcing is calculated with the help of an offline radiation model from simulations for PD and PI aerosol emissions.

The authors have addressed my critical remarks on a previous version of this text by including more discussion on other ice nucleation experiments with soot particles, and by clarifying a misunderstanding about the importance of contact nucleation in their model. These are certainly significant improvements. However, I still think that the ice nucleation parameterization used in this study and the ad-hoc modification applied to it are not suitable for the current purpose.

The below points are fundamental issues, which can only be addressed by thoroughly revising the treatment of ice nucleation in this model. I strongly encourage the authors to do so. The new treatment of hydrophobic, hydrophilic and hygroscopic soot is a very promising and novel development, which might even have other useful applications.

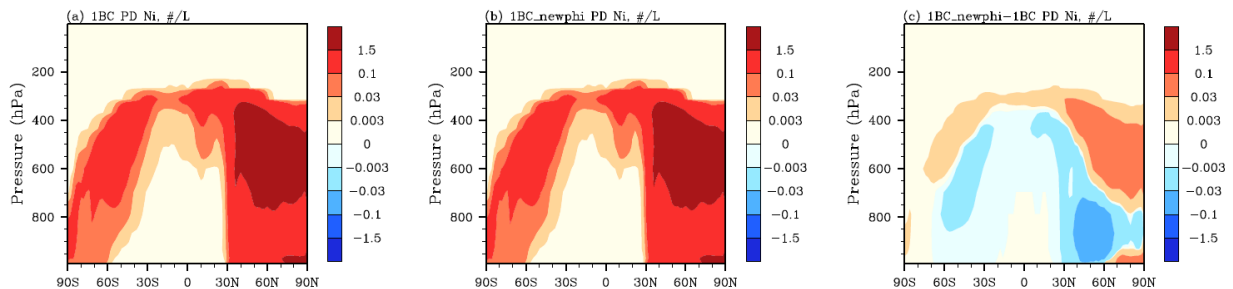
(Review comments in plain font, Replies in *italics*)

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## Major comments

- The parameterization by Phillips et al. (2008) has been criticized earlier for allowing too much ice nucleation on soot at high subzero temperatures. This could lead to an overestimation of the contribution to soot to mixed-phase cloud glaciation in the base case. It should be shown and discussed how large this contribution is in the CAM-IMPACT model. The anthropogenic forcing for both the 1BC and the 3BC-version of the model critically depends on this. A revised version of the Phillips et al. (2008) parameterization is now available (Phillips et al., 2012) in which immersion freezing by soot is suppressed at the warmest temperatures.

*Reply: We have implemented the revised Phillips et al. (2012) parameterization for soot aerosols, and compared the simulated ice number concentration with the previous version. Their differences are shown in the figure below.*



*It is true that immersion freezing by soot is suppressed at the warmest temperatures in the new Phillips et al. (2012) parameterization. No ice nucleation by soot is allowed at temperatures above -15°C. This will reduce the contribution of soot IN, as shown in figure (c) at middle and high latitudes where soot is present and the temperature is warm. Furthermore,  $\alpha_{BC}$ , which is the fractional contribution of BC IN to total IN in the baseline condition in Phillips et al. (2008, 2012) parameterizations, is reduced by a factor  $\Xi$  in the new parameterization due to the consideration of surface polarity and organic coatings. For our implementation of the Phillips (2012) parameterization, we assume that for the “average” fossil fuel burning soot in the 1-ffBC/OM scheme, there are some level of organic coating and surface polarity, and assume an average value of  $\Xi = 0.5$  ( $\alpha_{BC}$  is reduced by a factor of 0.5). This will also lead to less predicted soot IN with the new parameterization. In addition, the baseline surface area of soot is reduced in Phillips et al. (2012). This causes an increase the predicted soot IN, since the predicted soot IN is based on the ratio of soot surface area at the grid point to the baseline value. So for cold temperature regions where soot is allowed to nucleate ice in both the old and new parameterizations, the contribution of soot IN is increased in Phillips et al. (2012) compared to Phillips et al. (2008). The changes of ice number concentrations between the old and new versions of parameterization are generally within 10%.*

*We have added the following discussion to section 2.1: “Phillips et al. (2008) has been updated to suppress deposition/condensation/immersion freezing by soot above -15°C (Phillips et al., 2012). We have compared the current parameterization with the revised Phillips et al. (2012) parameterization for soot aerosols, and found that the changes of ice number concentrations between the old and new versions of parameterization are generally within 10%. The ice number concentration is lower with the new parameterization at warm temperature regions due to the suppression of soot ice nucleation. It is higher at cold temperature regions (where soot ice nucleation is not suppressed) due to the smaller baseline value of soot surface area. Comparison plots and discussions are shown in appendix A).”*

- Using the results of Koehler et al. (2009) for the mixed-phase temperature range, i.e. above -38C and at water saturation (as far as I understand, water saturation is prescribed in the model in mixed-phase clouds) is an unsupported extrapolation of the measurements. Koehler et al. (2009) studied deposition and condensation nucleation in the cirrus temperature regime by increasing RH at a given temperature in their instrument.

*Reply: You are correct, there are no measurements at the range of temperatures above -40C in Koehler et al. (2009). Although recent measurements of IN activity at -30C and above water saturation (in the immersion/condensation-freezing regime) for biomass burning- generated particles (Prenni et al., GRL, VOL. 39,2012) show that IN number concentrations are elevated by at least a factor of 2–3 over those typical of background air. (We have introduced this reference into the introduction).*

*We made a number of assumptions and stress in the paper that “We used the PH08 parameterization modified to treat the nucleation of ice in mixed-phase clouds by 3-ffBC/OM categories, which were chosen to match the hydrophobic, hydrophilic and hygroscopic categories of soot studied by Koehler et al. (2009). Although Koehler et al. (2009) did not measure ice nucleation at the higher temperatures experienced in mixed phase clouds, we altered the Phillips et al. (2008) parameterization to match the*

*Koehler et al. (2009) data at -40°C by increasing the frozen fraction by a factor of 10 for hydrophilic ffBC/OM, and reducing it by a factor of 0.15 for hydrophobic ffBC/OM. Then this altered Phillips et al. (2008) nucleation scheme is used to extrapolate the observed nucleation at -40°C to the warmer mixed-phase regime. In doing so, we preserve the ratio of frozen fractions at different temperatures in PH08. To treat the freezing of hygroscopic particles at higher temperatures, we made two assumptions. The first is that these particles are not able to freeze heterogeneously, and we exclude them as a heterogeneous IN. The second is that they are able to freezing heterogeneously, and we scale the frozen fraction predicted using PH08 by a factor of 15.*

*To clarify the issue, we correct the statement in the abstract as “Observational studies at cirrus temperatures ( $\approx -40^\circ\text{C}$ ) show that the hygroscopicity of soot particles can modulate their ice nucleation ability. Here, we implement a scheme for 3 categories of soot (hydrophobic, hydrophilic and hygroscopic) on the basis of laboratory data and specify their ability to act as an ice nuclei at mixed-phase temperatures by extrapolating the observations using a published deposition/condensation/ immersion freezing parameterization.” We have also changed the discussion of the laboratory experiments that the 3-ffBC/OM scheme is based on in the introduction and introduced our method of extrapolation of the Koehler measurements.*

In mixed-phase clouds, however, most air parcels reach water saturation at some higher temperature (lower altitude) and then cool further while ascending, maintaining water saturation (Wiacek and Peter, 2009). This means that the inhibited condensation on hydrophobic soot, which Koehler et al. (2009) also measured, might be irrelevant when the (immersion) freezing temperature is reached, as long as the particles have entered the droplets either due to higher peak supersaturations at cloud base or due to collision scavenging.

*Reply: We have estimated the fraction hydrophobic soot activated into cloud droplet to be about 15% in our model. From the estimate by Hoose et al. (2008), the contribution of collision scavenging is at most about one fifth of nucleation scavenging for BC and OM. Therefore, the inhibited condensation on hydrophobic soot still matters for the rest  $(100-15-15/5) = 82\%$  of the hydrophobic soot. This is now discussed in section 2.1 in the manuscript:*

*“All aerosols are assumed to be interstitial for the calculation of ice nucleation in our model. In reality, particles might have entered the droplets either due to higher peak supersaturations at cloud base or due to collision scavenging, in which case the effect of hygroscopicity on ice nucleation may be overruled. However, we have estimated the fraction of hydrophobic and hydrophilic soot activated into cloud droplet to be about 15% in our model. That from hygroscopic soot is about 20%. From the estimate by Hoose et al. (2008), the contribution of collision scavenging is at most about one fifth of nucleation scavenging for BC and OM. Therefore, the effect of hygroscopicity still matters for the rest (about 80%) of the soot particles.”*

• In addition, taking the activated fractions at  $\text{RH}_w=100\%$  is dangerous because (as also discussed by Koehler et al. (2009)) CFDCs resolve RH poorly in the supersaturated regime (several percent

uncertainty). In Petters et al. (2009), it was shown that the activated fraction for biomass burning particles at -30C increases at water supersaturation until a plateau was reached at about 9% supersaturation. I would expect a similar behaviour for soot.

*Reply: We acknowledge that the uncertainty of CFDC RHw is of order 3%. This is an implicit artifact of detecting IN using any CFDC type device or any ice nucleation device presently available (personal communication with Paul DeMott). We note that there is also an increase of ice nucleation fraction with increasing RHw to 110% in Koehler et al., (2009). However, we do not think it is likely that RHw could reach such a high value in mixed-phase clouds, since the presence of ice particles would draw down the vapor pressure. By taking the value at 100% RHw we are assuming that the relationship between nucleation fraction and RHw is linear, and we are taking the averaged value from 97% to 103%.*

*We have added the following discussion to section 2.2: “The uncertainty of the relative humidity w.r.t. water in the CFDC is about 3% (personal communication, P. R. DeMott, 2012). This is an implicit artifact of detecting IN using any CFDC type device or any ice nucleation device presently available (personal communication, P. R. DeMott, 2012). By using the published value of the fraction of soot nucleated at 100% ± 3% RHw we are assuming that the measured values represent the averaged value from 97% to 103% RHw. The data published by Koehler et al. show that the true fractions could be higher or lower by approximately ± 10 if the measured RHw differs by 3%”*

At RHw=100% and -40C, one likely measures only a (small) contribution from deposition nucleation and, if some fraction of the soot activates as CCN, the same fraction is expected to freeze homogeneously (-40C is already relatively far below the homogeneous freezing temperature). Both are not relevant for mixed-phase clouds.

*Reply: We are sorry for not understanding your reasoning about why only deposition nucleation and homogeneous freezing could be measured at -40C and RHw=100% by CFDC, and that (therefore) the measurement is irrelevant for mixed phase clouds, since condensation and immersion freezing should also be included as possible freezing mechanisms in mixed-phase clouds (the CFDC cannot distinguish these mechanisms). We think the reviewer is probably also concerned with the possibility that in nature soot can activate to drops at lower cloud levels and could then freeze via a homogeneous mechanism. The possibility for homogeneous freezing of activated CCN does exist, of course. However, for the hydrophobic and hydrophilic soot only a small fraction (about 15%) become droplets, so we think heterogeneous freezing needs to be considered in the model. In the Koehler et al. observations, heterogeneous freezing is the freezing mechanism due to the monotonic increase of frozen fraction with RHw, and the lack of correlation with the Koop line. For hygroscopic soot in their measurements, it is possible that homogeneous freezing was present, and that is why we have two sensitivity experiments. If hygroscopic soot freezes homogeneously, then they are not included in the heterogeneous freezing in mixed-phase clouds in our experiments.*

*We have added the following discussion to section 2.2: “For hydrophobic and hydrophilic soot, heterogeneous freezing is the likely freezing mechanism in the Koehler et al. (2009) experiments due to the monotonic increase of frozen fraction with RHw, and the lack of correlation with the Koop line.”*

- While the effect of sulfate coatings on soot ice nucleation properties in the mixed phase temperature regime is highly uncertain, because essentially no measurements are available for these conditions, there are several studies (cited above) investigating these effects at cirrus conditions. In my opinion this would be a more useful application of the newly developed aerosol model. However, it appears that the IN parameterization is kept unchanged for cirrus conditions. How is this done without introducing inconsistencies?

*Reply: The cirrus cloud ice nucleation scheme was kept unchanged in this paper, because we want to focus on the effect in mixed-phase clouds. This is now stated in section 2.2:*

*“The cirrus cloud ice nucleation scheme was kept as described in Wang and Penner (1% case) in this paper: this may be inconsistent, but we wanted to focus on the effect of ice nucleation in mixed-phase clouds.”*

*An updated cirrus cloud ice nucleation scheme that considers the effects of hygroscopicity of soot on ice cloud formation and nucleation will be described in another paper that is submitted, which focuses on effects in cirrus clouds.*

#### **Minor comments**

- The new aerosol scheme deserves more discussion in the results section. In particular, comparisons to observations would be appropriate, e.g. to the number fraction of internally mixed BC particles measured by Schwarz et al. (2008). Also some information on the BC burden in the model and how this is changed by the new treatment should be added.

*Reply: Comparisons of the 1BC/OM scheme to data from Schwarz et al were included in Koch et al. (2009), and the current comparison is similar. We now note this in section 2.1. It may be, however, that the reviewer wishes us to examine how each of the 3-BC/OM categories compare to Schwarz et al. Schwarz et al. (2008) determine internally mixed BC particle by analysis of the laser light scatter from the particle as the laser heats it. “The primary method for identifying coated (or internally mixed) BC particles is based on recognizing any clear reduction in the scattering signal measured for a BC particle occurring more than 0.4  $\mu$ s before the refractory particle reaches its vaporization temperature (onset of incandescence).” (Schwarz et al., 2008) This is different from the method we use to distinguish hydrophobic, hydrophilic, and hygroscopic BC, which is by the number of monolayer of coatings. It is unclear to us how to convert these two methods and make a meaningful comparison.*

*We have added the burden and lifetime from the 1-ffBC/OM scheme to Table 2, and compared them to those from the 3-ffBC/OM scheme in section 3.1: “the lifetime of soot particles using the 3-ffBC/OM scheme is decreased compared to that in the 1-ffBC/OM scheme. This is mainly driven by the increased wet removal rate for the hygroscopic particles, since the sulfate coating thickness is not diluted by newly emitted hydrophobic soot through the process of calculating an “averaged” coating thickness as in the 1-ffBC/OM scheme. As a result, the total fossil fuel combustion soot burden is smaller in the 3-ffBC/OM scheme (Table 2).”*

- The ice nucleation parameterization, in particular if a number of changes are applied, should be shown graphically (e.g. as activated fraction for a given particle size as a function of RHw and T).

*Reply: We have added a new Figure 2 that shows the frozen fraction of soot as a function of temperature for the 1-ffBC/OM scheme and 3-ffBC/OM scheme.*

- Koehler et al. (2009) studied five different soots, three of which are selected for this study. Why not the other two? This seems arbitrary.

*Reply: We have added the following discussions to section 2.2 to address this question:*

*“All of the soot samples used in Koehler (2009) studies were first characterized using three hygroscopicity categories, using the concept of quantification of water uptake (Popovicheva et al. 2008b). There are five different soot samples. Aircraft engine combustor (AEC) soot is the only soot sample characterized as hygroscopic, so it was chosen as the representative for hygroscopic soot in our study. Thermal Soot (TS) soot is hydrophobic. Graphitized thermal soot (GTS) soot is produced by heating the TS soot to ~ 3000 °C to remove any impurities from the surface and graphitize the structure, and is extremely hydrophobic. We think that the soot emitted from fossil fuel combustion is likely to have impurities and unlikely to be extremely hydrophobic. Therefore TS soot was selected as the representative for hydrophobic soot for this study. Thermal oxidized soot (TOS) soot and TC1 soot (TC1 kerosene flame soot) are both characterized as hydrophilic. However, TC1 soot is typically composed of agglomerates of 20-50 nm particles, is highly micro-porous and is subject to swelling phenomenon. Therefore the hydrophilic properties of TC1 soot may not be solely explained by the surface properties. So TOS soot was selected as the representative for hydrophilic soot for this study. ”*

(On a side-note, it took me a long time to figure out which data were actually used. This should have been stated more explicitly.)

*Reply: We apologize for not being clearer initially. All the data for frozen fractions at 100% RHw and -40 °C were taken from Table 1 in Koehler et al., (2009). We have added this as well as the above explanation to the paper.*

- The authors state that the Bergeron-Findeisen process is included in the offline simulations. It is unclear to me how this is done. Glaciation of clouds via the BF-process can lead to precipitation and cloud dissipation, but how can this information be kept in the following timesteps in an offline model?

*Reply: The short answer is that the change of precipitation and cloud dissipation is not included in the offline model. The advantage of using an offline model is that we can decide ourselves what is fixed and what is not. Most meteorology variables are read-in and fixed in the offline model, but we choose to predict the ice number concentration from nucleation, and the ice/liquid number/mass change from*

*contact freezing and Bergeron-Findeisen process. So by saying that the Bergeron-Findeisen process is included in the offline simulations, we only mean that we included the ice/liquid number/mass change due to the Bergeron-Findeisen process. We have made this clearer in the paper by adding to section 2.1: “In the offline radiation model, we predict the ice number concentration from nucleation using aerosol concentrations from an on-line calculation that are read-in. The ice/liquid number/mass concentration change from contact freezing and the Bergeron-Findeisen process (the conversion of liquid to ice) was also implemented, due to its importance to radiative forcing (Storelmo et al., 2008b). Other meteorology variables are fixed and no further processing of ice particles takes place (no sedimentation, coagulation, or precipitation formation).”*

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